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Finding Commercial Uses for the Coal Acids

By

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When we began our work on the mixed acids obtained by the caustic-oxygen oxidation of bituminous coal, our first concern was to find commercial applications for them. Just as with any other research chemical, the important question was, "What are they good for?". Basically, the coal acids are a complex mixture of polyfunctional aromatic acids with benzene, naphthalene, and biphenyl as the chief nuclei. (1) The average molecular weight is about 270 and the average equivalent weight about 81. Therefore, the average functionality is about 3.3. They are made by oxidizing a suspension of bituminous coal in aqueous sodium hydroxide by means of gaseous oxygen at a temperature of about 290°C. and a total pressure of about 1800 p.s.i.g. (2) In this paper, I plan to discuss our general plan of attack on the problem of finding out "What are they good for?".

INITIAL WORK

The most obvious line of attack and the one generally used at the outset in problems of this nature is to try to use the new chemical in applications where similar materials are now being used. A model compound of similar structure is selected and then one systematically attempts to substitute the new compound for this compound in all the areas where it is being used. The only polyfunctional aromatic acid of much commercial importance is phthalic acid and so it is natural to select this acid as our "model compound". This leads us to an investigation of the possible use of the coal acids in plasticizers, plating baths, synthetic lubricants, alkyd resins, and the like. We investigated these uses as did other investigators a good deal prior to us. (3)(4) (5) In general, however, this approach was not very profitable mainly because the coal acids are really not very similar to phthalic acid. In the first place they are a complex mixture rather than a single chemical species. In addition, they are water-soluble, rather dark colored, and have higher functionalities and molecular weights than does phthalic acid. Because of this, the coal acids appear to be inferior to phthalic acid in all the applications where phthalic acid is commercially used.

SEPARATION

The next logical line of attack on this problem is to attempt to separate the mixture into its components. If this is not feasible, perhaps the mixture could be fractionated into simpler mixtures or perhaps at least the dark colored components could be removed. Previous investigators had attempted to separate the mixture by distillation of the esters and by solvent fractionation. (6) We investigated these methods (7)(8) and also investigated a fractionation based on differences of acid strengths (8) and even partition chromatography. (9) None of these methods was suitable for the commercial separation of the components and only the fractionation based on the different acid strengths appeared to be of any commercial importance. With this method, a reasonable fractionation can be obtained as can be seen from Figure 1 but the fractions are still dark-colored and are still complex mixtures. The dark-colored components could not be removed although some of the fractions obtained by the distillation of the esters, chromatography, and solvent fractionation were lighter in color

than others. Treatment of the mixture with hydrogen, hydrogen peroxide (10), carbon, and sodium hypochlorite were all quite ineffective although the hypochlorite treatment did give some improvement.

#### THERMOSETTING RESINS

After the only very limited success of these two lines of attack, some new point of view was required so we then began to look at the coal acids as a basically new and different chemical and began to try to exploit its unique properties. The properties that seemed the most important were the high functionality, aromatic character, and perhaps the water solubility. Although many applications were investigated from this point of view, I will discuss only the ones that appeared to be of the most interest.

The high functionality of the coal acids suggested that they might be useful in a highly crosslinked, thermosetting resin. Their aromatic character led us to believe that they could also contribute good heat stability and good resistance to oxygen attack. Therefore, we felt that we could, perhaps, make good, relatively heat-resistant binder resins from them and we began to look for applications requiring resins of this kind. In addition, the fact that the acids were water-soluble allowed the uncured mixture or the partially cured resin to be applied directly from a water solution. This led us to investigate these coal acid resins as foundry binders, plywood and hardboard binders, glass fiber binders, etc. Two of the following papers will be concerned with these applications so I will not go into them any further.

#### WARP SIZE

Another unique property of the coal acids is their ability to form films. An aqueous solution will dry to a rather tough, pale-yellow film. This behavior is unusual for a material of molecular weight on the order of 270. The viscosity behavior of a concentrated aqueous solution, however, provides an insight into the reason for this property. From Figure 2 it can be seen that the coal acids in dilute solution behave as individual monomeric units of about 270 molecular weight but as the solution becomes more concentrated, the viscosity increases more rapidly than can be accounted for by just the increased concentration. The molecular weight increases as the concentration increases until at very high concentrations we have, in effect, a high polymer. This is probably due to the formation of hydrogen bonds as the monomeric units are brought closer and closer to each other when the solution becomes more concentrated and can be considered as actually a kind of reversible polymerization. Perhaps then, the coal acids could be used in applications where water-soluble polymers are used. We investigated several of these applications and the most promising appeared to be textile warp sizing. This specific application will be discussed in a following paper so I will not say much about it but I would like to emphasize the fact that this use is based on the unique physical behavior of the coal acids and would not be expected on a basis of the physical properties of other known aromatic acids.

#### SLURRY THINNING

Another application based on the unusual water solubility of the coal acids is that of slurry thinning. It was already known that the sodium salts of the coal acids were useful as slurry thinners for weighted drilling muds. (11) Normally only the salts of large molecular weight organic acids have the required solubility for this application but in this case the acids themselves can be used. The coal acids themselves have shown a much wider applicability than did their sodium salts. For instance, the coal acids are useful for thinning ordinary drilling mud as well as weighted drilling mud. Figure 3 shows the viscosity of bentonite drilling mud as a

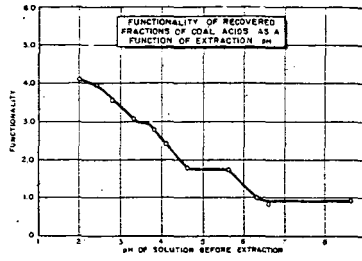
function of the amounts of both the coal acids and their sodium salts. This again is an example of a use based on the unique properties of the coal acids.

#### CONCLUSIONS

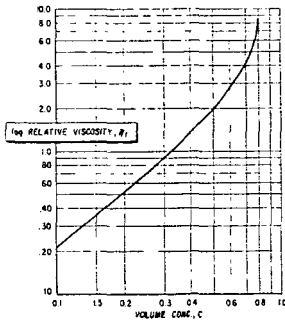
In conclusion, I would like to re-emphasize the fact that very often, as in this case, the more conventional ways of investigating the utility of a new material may be unproductive but a fresh point of view may provide us with an important new use based on one or more unique properties of the material. In the case of the coal acids, their use in thermosetting resins, as water-soluble film formers, and as slurry thinners are all based on unique properties and would not be predicted on a basis of the properties of other aromatic acids.

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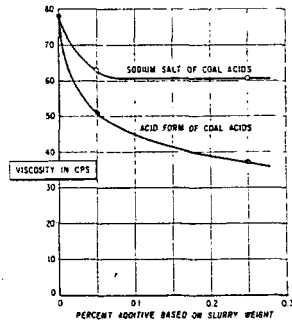
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VISCOSITIES OF AQUEOUS COAL ACID SOLUTIONS AS A FUNCTION OF CONCENTRATION



VISCOSITY OF A 7% BENTONITE SLURRY AS A FUNCTION OF AMOUNT OF ADDITIVE



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Coal Acids -- A Potential Warp Size  
for Continuous Multifilament Yarns

By

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Aqueous solutions of the mixture of water soluble aromatic polycarboxylic acids<sup>(1)</sup> produced by the caustic oxygen oxidation of coal will dry to form a rather tough water soluble film. One possible market for such a material is as a warp size in the textile industry. In this paper we would like to summarize the results of our evaluation of the coal acids for this use.

A warp size can probably best be described as a water soluble coating applied to the warp yarns to increase loom efficiency during weaving. The size is applied to the yarns from an aqueous solution and must be sufficiently water soluble so that it can be completely removed by a dilute detergent solution. In addition, the size must have good adhesion to the yarn and be sufficiently pliable to protect the warp yarns from the flexing, abrasion, and other stresses of the weaving operation.

Just as the above definition implies, the only absolute method for evaluating sizes is to conduct rather extensive weaving trials. However the cost of such a test necessitates some type of preliminary testing to establish a high probability of success. Potential sizes can be evaluated in the laboratory if one simplifies the problem somewhat and looks at the desirable physical properties which are either afforded or enhanced by the presence of a suitable size on the yarn. In the case of a continuous multifilament yarn these properties would include unitization of the yarn and abrasion resistance. It is also necessary to determine if the size has any degradative effects on the yarns physical properties in addition to establishing the ease of application and removal of the size. By comparing the effects of an experimental material and a commercially accepted size it is possible to get an indication of the probability that the experimental material may have for success in a weaving trial.

The coal acids were first evaluated on continuous multifilament nylon yarn. There were two principal reasons for choosing this yarn. First, it is well known that materials having a low pH give the best adhesion to nylon fibers and second, the low viscosity of the size solution suggested that the size might not "lay" the protruding fibrils of a staple yarn in the desired manner. In this evaluation the widely accepted polyacrylic acid size (Acrysol A-1) manufactured by Rohm and Haas was chosen as the control with which the coal acids were compared.

#### Ease of Application and Removal

Observations made during the preparation of sized samples for testing using the single-end slasher shown in Figure 1 indicated that there would be no problems in applying the coal acid coating to the yarn. While the use of a colored material as a warp size could possibly have certain advantages it has the one major disadvantage in that it must be completely removed from the woven fabric.

Two general methods were used to determine whether the coal acids could be satisfactorily removed from the yarn. The first of these methods was based on the acidic nature of the size. Sized samples of yarn were rinsed with a stream of water for about ten minutes and then after drying were titrated with dilute base to determine the amount of residual acid. The results of this test indicated that the amount of coal acids left on the yarn was below 0.05% size pick-up. A more accurate method was worked out based on the color of the coal acids. In this method samples of the sized yarn which had been washed in an aqueous solution of 0.25% Triton X-100 and 0.25% tetrasodiumpyrophosphate were wound on plastic chips and the color of the yarn determined on a Hunter Color and Color Difference Meter (H. A. Gardener Laboratories, Bethesda, Md.). Samples of yarn sized with Acrysol A-1 and unsized yarn were tested in a similar manner. The results of this evaluation are shown in Table I.

TABLE I  
HUNTER COLOR AND COLOR DIFFERENCE METER DATA

Sample	$R_d$	a	b
Porcelain Standard	77.0	-0.2	+1.8
Unsize Yarn	52.8	-3.0	+3.0
Washed Yarn (Acrysol A-1)	54.9	-2.7	+3.8
Washed Yarn (Coal Acids)	52.6	-3.0	+3.1
Washed Yarn (Coal Acids)	53.3	-3.0	+3.2

KEY: The  $R_d$  column indicates the per cent reflectance.  
The negative numbers in the 'a' column indicate the degree of blueness and the positive numbers in the 'b' column indicate the degree of yellowness.

Although it was impossible to exactly duplicate commercial methods of scouring or size removal, the data in Table I indicates that the coal acids can be completely removed from the yarn.

#### Yarn Degradation Studies

In certain cases it may be necessary to store a sized warp for prolonged periods of time. Therefore, it is essential that the size have no adverse effects on the physical properties of the yarn. The tensile strength and per cent elongation of nylon yarn which had been aged after being sized with Acrysol A-1 and coal acids were determined and found to be comparable.

#### Abrasion Tests

The most widely accepted method of laboratory evaluation of experimental sizing materials is that of determining the abrasion resistance of the sized yarn. However, the type of abrader and test may vary considerably with the investigator and the type of yarn used (2). The method which we employed in evaluating the coal acids, and which appears to work quite well on continuous multifilament yarns, is based on the Duplan Cohesion Tester (Geier and Bluhm Inc., Troy, N. Y.). See Figure 2. The purpose of a warp size is to reduce the number of breaks in the warp yarns during weaving but this yarn break point is not necessarily a good end point on an abrasion tester. This is particularly true with continuous multifilament yarn where the yarn itself may not break from abrasion alone for several thousand cycles while a good size may well be completely destroyed after 50 cycles. For this reason the "fray-point" was chosen as the end point on the Duplan Cohesion Tester because it clearly shows the point at which the size film is destroyed. The use of this end-point, which is shown in Figure 3,

enables one to measure the degree of unity and abrasion resistance imparted to the yarn by the size. By testing samples of yarn having varying percentages of size pick-up we were able to compare the properties of the commercial and the coal acid sizes. The results of this evaluation are shown in Figure 4. The data shown in Figure 4 indicates that the coal acids and Acrysol A-1 afford a comparable amount of protection to the yarn.

The results of the above tests indicate that the coal acids might be a good warp size for nylon multifilament yarns and suggests further testing in the form of a weaving trial.

#### Other Types of Yarn

On the basis of the favorable results obtained on nylon, the coal acids were also evaluated on other types of continuous multifilament yarn. In each case a commercial size was used as a control. Evaluations were carried out on Dacron, Orlon and cellulosic type yarns and in general the results obtained were very similar to those obtained on nylon. The results of the abrasion resistance studies on these yarns are shown in Figures 5, 6, and 7. These results indicate that perhaps the coal acids might find rather wide application as a warp size for continuous multifilament yarns.

#### Weaving Trials

After a small scale weaving trial was conducted successfully on equipment located in the Midland Division a larger and more thorough trial was carried out at North Carolina State School of Textiles, Raleigh, N. C. In evaluating the coal acids in these weaving trials every attempt was made to handle the experimental material in the same manner as it would be handled commercially. These weaving trials were carried out on continuous multifilament nylon yarn and here again the evaluation was conducted in such a manner that the coal acids could be compared directly with the Acrysol A-1 size.

In general the results of the weaving trial followed very closely those of the laboratory evaluation. It was noted during the sizing operation that the coal acid sized warp parted much easier and subjected the yarn to much less strain than did the commercial size. While the length of the weaving trials was not sufficient to calculate with certainty the efficiency of the sizes there were fewer yarn breaks attributable to 'size failure' in the coal acid warp than there were in the Acrysol warp.

It was in the last stages of the weaving trial, that is the scouring step, that the only serious problem was encountered. During this step the sized fabric was accidentally exposed to live steam before the scouring was started. It was found that temperatures in this range were sufficient to "set" the coal acids or actually cause chemical combination with the yarn which prevented the complete removal of the color from the fabric. Further testing in the laboratory indicated that temperatures of 180°F. or greater would cause varying degrees of discoloration in direct proportion to the time the temperature was maintained. It is not uncommon for slasher drying can temperatures to be maintained in this range but the coal acids have the advantage that their high fluidity will allow drying at lower temperatures (<160°F.) while maintaining normal slasher speeds. The discoloration would probably also be lessened when the coal acids are used on another fiber where the ionic association of the reactive groups in the fiber and size are not so great.

Summary

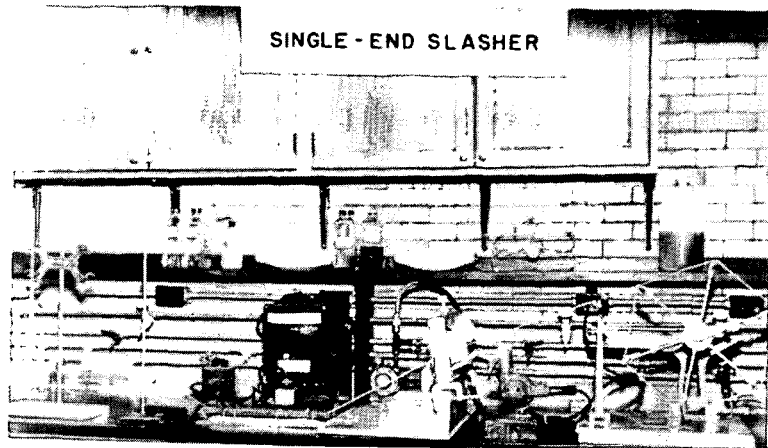
The coal acids form water soluble films which may be useful as warp sizes for continuous multifilament yarns. The films appear to impart as much or more abrasion resistance to a wide range of multifilament yarns as commercially accepted sizes. The only apparent problem is the tendency of the coal acids to react with, and thereby discolor the yarn at elevated temperatures.

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CONE → TENSION  
POST → SIZE BATH → WRINGER → DRYER → YARN REEL

FIGURE 1

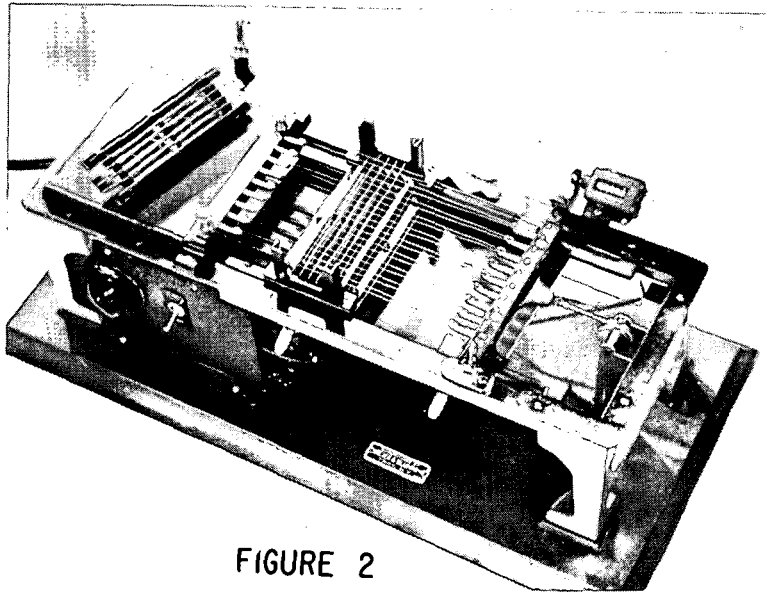


FIGURE 2

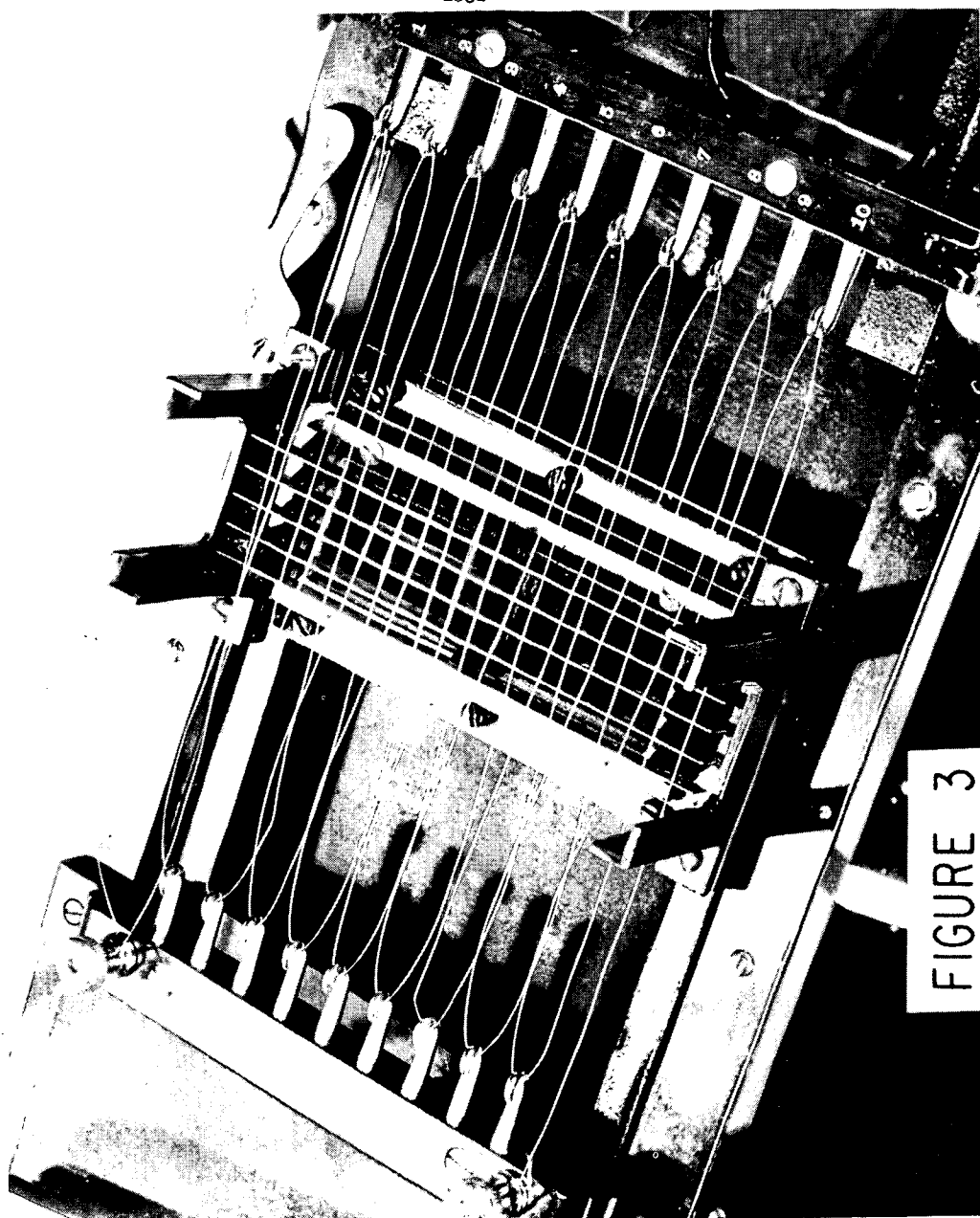


FIGURE 3

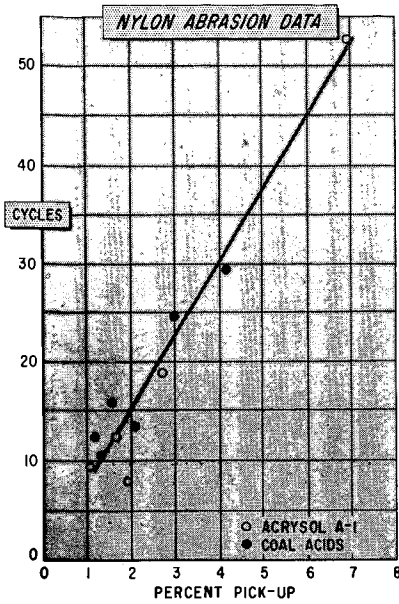


FIGURE 4

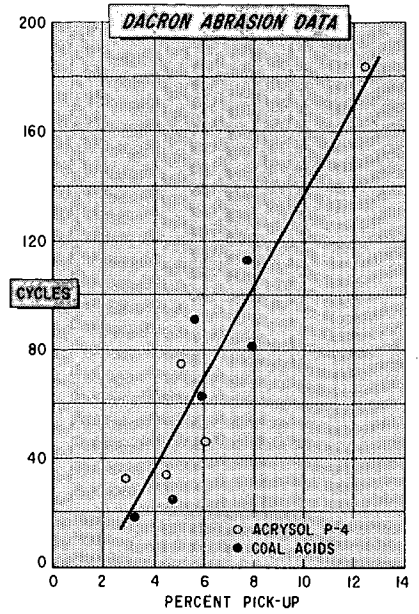


FIGURE 5

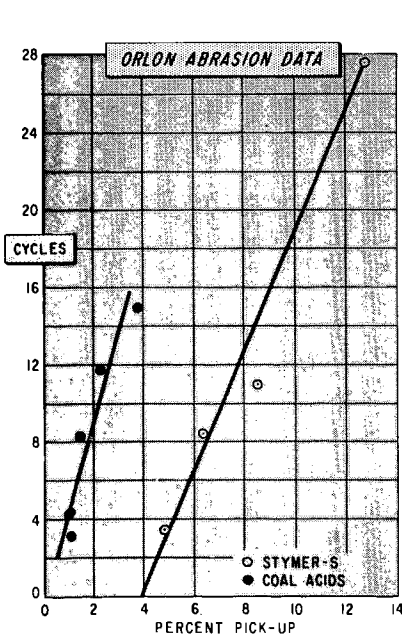


FIGURE 6

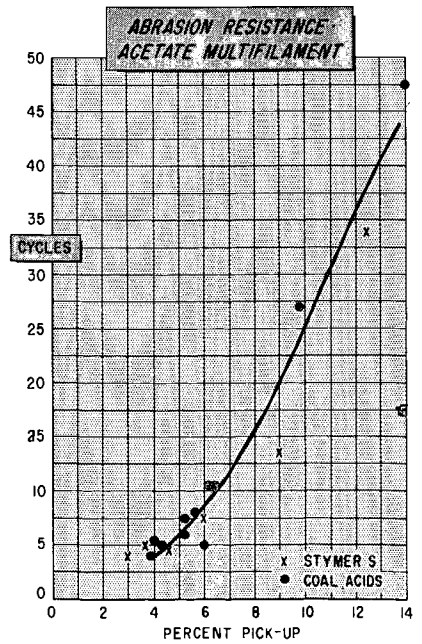


FIGURE 7

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Coal Acids - An Intermediate For Thermosetting Resins

By

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INTRODUCTION:

Gaseous oxygen oxidation of an alkaline slurry of bituminous coal yields a mixture of water soluble aromatic polycarboxylic acids (1). These coal acids have been shown to have three principle aromatic ring systems, namely benzene, naphthalene and diphenyl (2). The mixture is strongly acidic and has an average functionality of approximately three.

The coal acids afford an interesting and relatively inexpensive raw material. One specific use of these acids is in the preparation of thermosetting resins. The large markets for resins of this type provided an interesting field of investigation and efforts to develop these resins are outlined in this paper.

Coal acids can be reacted with an alkanolamine, alkylene oxide, polyhydroxyl compound or polyamine to give thermosetting resins. Variation of reactants, the equivalents used or the reaction conditions allows a wide spectrum of resins with varying properties. The polyamide, polyester or combination of functional groups possible in these resins are shown in examples 1-5. In examples 1, 2 or 3 an equivalent of hydroxyl or amine reactant

- (1)  $R(\text{COOH})_3 + \text{HN}(\text{CH}_2\text{CH}_2\text{OH})_2 \longrightarrow R(\text{COOCH}_2)_2 (\text{CONCH}_2-)$
- (2)  $R(\text{COOH})_3 + \text{HOCH}_2\text{CH}_2\text{OH} \longrightarrow R(\text{COOCH}_2)_3$
- (3)  $R(\text{COOH})_3 + \text{H}_2\text{N}(\text{CH}_2)_n\text{NH}_2 \longrightarrow R(\text{CONCH}_2-)_3$
- (4)  $1 \text{ eq. } R(\text{COOH})_3 + 1 \text{ mole } \text{NH}(\text{CH}_2\text{CH}_2\text{OH})_2 \longrightarrow R \left[ \text{CON}(\text{CH}_2\text{CH}_2\text{OH})_2 \right]_3$
- (5)  $R(\text{COOH})_2 + \text{CH}_2\text{CH}_2\text{O} \longrightarrow R(\text{COOH})(\text{COOCH}_2\text{CH}_2\text{OH})$

is used for each carboxylic acid equivalent, while in example 4 one mole of diethanol-amine is used per equivalent of acid group. The latter resin will have free hydroxyl groups which could then be crosslinked. Use of a large excess of a glycol reactant with the coal acids also yields a resin with free hydroxyl groups. The preparation of a partially reacted ester with free carboxylic acid and hydroxyl groups is shown in example 5. The resultant water soluble resin intermediate gives a crosslinked structure when cured at elevated temperatures.

A. Preparation and Chemistry of the Resins

Alkanolamine, Polyhydroxyl and Polyamine Resins

The mixture of aromatic polycarboxylic acids (coal acids) obtained from the Coal Research Laboratory of the Carnegie Institute of Technology in Pittsburgh was used in the preparation of some of the resins. The average molecular and equivalent weights are 270 and 82 respectively giving an average carboxylic acid functionality of 3.3. Many of the later resins were prepared from coal acids made at the Dow Chemical Company. These coal acids were shown by equivalent and molecular weight determinations to be similar to the material obtained from the Carnegie Institute of Technology.

A novel and useful feature of these resins is that a mere physical mixture of the coal acids and other reactant in water may be applied directly to the substrate to be bonded. This method of application eliminates the hazard and expense of

organic solvents in commercial applications. The resin adduct in a concentration range of 50-80% solids gives a water solution of workable viscosity and good film forming properties.

A partially cured but still water soluble coal acid resin was prepared from the coal acids and monoethanolamine by heating equivalent amounts of the reactants at 170°C. for 3 hours. Approximately 85% of the water of esterification slowly distilled off giving on cooling a water soluble solid. Titration of this material revealed the presence of nearly all the original amine salt groups. Use of a di or trialkanolamine however yields water insoluble products because of excessive crosslinking of the hydroxyl group.

Another partially cured, but still water soluble resin can be prepared from the coal acids and pentaerythritol. A suspension of an equivalent of pentaerythritol in a 70% solids solution of one equivalent of coal acids in water was stirred and heated at reflux for 3 hours. The resultant solution on titration showed 27% esterification of the pentaerythritol, while after 24 hours of reflux the esterification approaches an equilibrium value of 40%. The partially advanced resin is a viscous solution which does not exhibit any precipitation on standing for prolonged periods.

#### Alkylene Oxide Derived Resins

Ethylene, propylene and butylene oxide have been reacted with the coal acids in a dioxane media to produce partially reacted esters containing carboxylic acid and hydroxyl groups. These products, which are water soluble in concentrated solutions, can be cured to give a thermosetting resin. The resin of primary interest involves the reaction of one mole of ethylene oxide with two equivalents of coal acids as shown in example 5.

The alkylene oxide addition is generally allowed to proceed until one half of the carboxylic acid groups have reacted giving a resin intermediate which on final cure has no reactive groups. Wide deviation from the 50-50 acid hydroxyl group ratio may give a thermoplastic resin on final cure.

Ethylene oxide adducts with equivalent weights in the range of 162 to 328 have been prepared as have propylene oxide adducts with equivalent weights of 170-440. Reaction with butylene oxide is slower and required the addition of a small amount of sulfuric acid and additional heating at 60°C. to give an adduct with an equivalent weight of 223.

#### Resin Compatibility with Phenol - Formaldehyde Resins

Preliminary work has shown that various coal acid resin adducts are compatible with the "A or B stage" water borne phenol - formaldehyde resins. However the amine salt character of the alkanolamine or polyamine - coal acid resins limit their compatibility with alcohol borne phenol - formaldehyde resins.

Laboratory investigation has indicated that an actual reaction can occur between the coal acids and the phenol - formaldehyde resin.

Various amounts of coal acids were mixed with both "A" and "B" stage phenol - formaldehyde resins and the mixtures cured. The cured resin mixtures were then titrated in order to determine the amounts of the coal acids that had been incorporated into the cured resin structure. It was found that the "A stage" resin could combine with approximately 43% of its weight of coal acids but the "B stage" resin only 7% of its weight. This can be explained by the fact that the "A stage" resin contains a much larger proportion of free methylol groups than does the "B stage" resin.

## B. Reaction Rate Studies

Reaction rate studies of the alkanolamine - coal acid resin adducts have afforded information concerning the relative rates of ester formation as compared with amide - imide formation. The usual methods for kinetic studies are useless in this case because of the highly crosslinked and insoluble nature of the coal acid resins. The most satisfactory solution to the problem was to cure weighed samples of the resin adduct on squares of aluminum foil which were floated on the surface of a Wood's metal bath controlled at a fixed temperature. The resin samples were prepared from a mixture of 1:1 equivalent of alkanolamine - coal acids containing 10% water. The sample after cure was digested in a methanol - water solution and titrated with 1N sodium hydroxide. A plot of pH vs. milliequivalents of alkali revealed two points of inflections, one occurring at approximately pH 7 and indicating free carboxylic acid group and the second inflection point at pH 9.5-10.5 which corresponded to the amine salt component.

Samples were run for various time intervals and the milliequivalents of un-reacted carboxylic acid groups and/or amine salt groups plotted vs. the cure time in minutes. The semilogarithmic plot approximated a straight line suggesting a first order reaction. This behavior is reasonable, since both reactants are combined into one molecular species by means of the amine salt formation.

A typical plot of an alkanolamine - coal acids reaction is shown in Figure 1. In this case samples of a 1:1 equivalents formulation of the diethanolamine - coal acid resin were cured at 265°C. Line A shows the disappearance of the combined free carboxylic acid and amine salt groups, line B the esterification rate while line C is the rate of formation of the amide or imide. The reaction rate constants and half lives of the mono, di and triethanolamine - coal acid resin reactions are shown in Table I. The slower rates exhibited by the di and triethanolamine resins are probably due to steric hinderance. Use of an acidic catalyst gave the expected reaction rate increase.

Cure rates of the diethanolamine - coal acid resin were determined for temperatures in the range of 240-300°C. to give the Arrhenius plot shown in Figure 2. The slope of the plot is only slight in this temperature range while determinations at 150 and 210°C. gave rate constants far below this range. These lower rate constants may be partially due to a lower heating efficiency of the experimental setup at these temperatures or perhaps indicate a reaction rate threshold effect.

Preliminary work has shown that reaction rates of the coal acid - glycol resins can also be determined provided a lower temperature, e.g. 150°C., is used in order to reduce the evaporation losses of the glycol. Figure 3 is a plot of the reciprocal of the square of the carboxylic acid concentration vs. time as obtained with a coal acid - diethylene glycol resin system. Since the reactants have the same initial concentration, the resultant straight line plot indicates a third order reaction. This is in accord with the mechanism of an acid catalyzed esterification. The catalyzing acid in this reaction is the coal acids because of the strong acidic nature.

A rate study of the coal acid - pentaerythritol resin adduct has proven interesting since the results indicate a first order reaction similar to the alkanolamine resins. The reactants were heated in water to give a partially esterified resin which on titration showed 18% advancement. Samples of the 75% solution were then cured in the normal manner at 230°C. Use of the titration procedure gave a plot shown in Figure 4. A first order reaction is reasonable if one considers that a large portion of the partially cured resin adduct is in the form of a molecular species having both acid and hydroxyl groups. Thus the reaction in this study would be primarily an intramolecular polycondensation and first order. Calculation

of the first order reaction rate constant for this reaction gives a value of 0.175 minutes<sup>-1</sup> and a half life of 3.95 minutes respectively.

#### Saponification of Coal Acid Resins

A brief look at the saponification rates of some of the coal acid polyesters may be of interest at this point. The completely cured resin (225°C. for 2 hours) ground to less than 250 mesh was suspended in N/10 sodium hydroxide. The suspension was stirred at room temperature and portions removed at intervals for titration. The saponification rates of the diethanolamine, ethylene glycol and pentaerythritol resins of the coal acids are shown in Figure 5. The lower saponification rates of the diethanolamine and pentaerythritol resins can be explained by steric hinderance. Saponification of the pentaerythritol resin by several different concentrations of sodium hydroxide shows that the rate and extent of degradation is proportional to the alkali concentration.

#### C. Physical Properties of Coal Acid Resins

##### 1. Physical Strength

Sand briquettes were used as the test media in determining the physical strength of the coal acid resins. The one inch thick sand briquettes were of the figure eight shape and identical to the form adopted by the A.S.T.M. for evaluation of foundry molding sands. Table II lists the tensile strengths of the various resin bonded sand briquettes. All the resins were physical mixtures of one equivalent coal acids and one equivalent reactant in water unless otherwise stated.

The resins in order of decreasing strength are the ethylene oxide adduct, pentaerythritol, glycol and alkanolamine adducts. The alkanolamine type resins can be considerably overcured without impairing their strength, while a glycol resin bonded briquette overcured for 5 minutes at 260°C. suffers a strength loss of some 20%.

##### 2. Heat Stability of Cured Coal Acid Resins

Investigation of the coal acid resins as a glass fiber binder prompted a study of the resin's heat stability. Briefly, the method of test consisted of suspending a powdered sample of the cured resin in a wire screen holder placed in a vertical furnace. A thermocouple placed in the sample continuously measured the temperature of the sample as the furnace temperature was gradually increased and the resin started to burn. The slope of the combustion temperature curve between 700 and 1100°F. was used to express the rate of resin combustibility. The reciprocal slope ( $\Delta \text{ temp.} / \Delta \text{ time}$ ) was used in order to obtain numbers greater than one. If no resin combustion takes place under the conditions used the resin sample temperature will not exceed 700°F. Therefore, the temperature line between 700 and 1100°F. would be due to the resin heat of combustion.

A second heat stability test applied to our resins determined the critical temperature at which the resin would completely burn without added heat. The overall heat stability of the particular resin was shown by combining the slope factor and critical temperature into the expression  $\frac{\Delta \text{ temp.} / \Delta \text{ time}}{\text{critical temp.}}$ . Some of our combustibility data from this slope method are given in Table III.

The resins in order of decreasing heat stability are diethylene-triamine, diethanolamine, ethylene glycol adduct and phenol-formaldehyde resins. The heat stability of the coal acid - polyamine resin is similar to some melamine type resins.

#### CONCLUSIONS:

The coal acids undergo polycondensation reactions with alkanolamines, polyhydroxyl or polyamine reactants to give thermosetting resins. Proper choice of reactants, reactant ratios and reaction conditions allows the preparation of a large number of resins with varying properties. The resin adducts may be simple mixtures of the reactants in water or a partially reacted resin which is still water soluble.

The cure process of the various resins can be followed by titration of the still unreacted carboxylic acid or amine salt groups. Thus a method is available for the evaluation of various reactants and conditions in the preparation of the coal acid resins.

Physical properties of these resins that have been studied include their strength and heat stability. The resins in order of decreasing strength are the ethylene oxide adduct, pentaerythritol, glycol and alkanolamine - coal acid resins. Many of the coal acid resins have physical strengths sufficient to allow their use as resin binders. The heat stability of several coal acid resins have been found to be superior to a typical "A stage" phenol - formaldehyde resin.

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Montgomery, R. S., Holly, E. D., ibid. 36 (1957) 63



TABLE I

CURE RATES OF ETHANOLAMINE - COAL ACID RESINS AT 265°C.

Resin	Total		Ester		Amide/Imide	
	k min <sup>-1</sup>	t <sub>1/2</sub> min.	k min <sup>-1</sup>	t <sub>1/2</sub> min.	k min <sup>-1</sup>	t <sub>1/2</sub> min.
Monoethanolamine	1.22	0.57	1.67	0.42	0.82	0.85
Diethanolamine	0.68	1.02	0.73	0.95	0.62	1.12
Triethanolamine	0.41	1.68	0.46	1.50	0.28	2.44
Diethanolamine	0.87	0.80	0.96	0.72	0.72	0.98
With 5% poly H <sub>3</sub> PO <sub>4</sub>						

TABLE II

TENSILE STRENGTHS OF COAL ACID RESIN BONDED SAND BRIQUETTES

Reactant (6% green solids)	Cure Conditions	Tensile Strength, psi.
Monoethanolamine	15 min./260°C.	128 psi.
Diethanolamine	" "	458
Triethanolamine	" "	302
Ethylene glycol (1)	" "	562
Diethylene glycol	" "	690
Propylene glycol	10 min./260°C.	464
Dipropylene glycol	22 min./260°C.	494
Triethylene glycol	18 min./260°C.	580
Ethylene oxide (2)(3)	40 min./225°C.	830
Pentaerythritol (4)	45 min./250°C.	738

- Footnotes: (1) 5.5% resin solids  
 (2) Coal acid - ethylene oxide adduct at approximately 50% reaction.  
 (3) Thermoplastic after 30 min. cure  
 (4) Resin composed of 1 eq. coal acid and 0.9 eq. of pentaerythritol and reacted to 16% esterification.

TABLE III

COMBUSTIBILITY RATES OF CURED RESINS

Resin or Coal Acid Reactant	Temp.	Critical	Slope	x 10 <sup>3</sup> min <sup>-1</sup>
	Time (°F. min <sup>-1</sup> )	Temp. °F.	Critical Temp.	
"B stage" phenol-formaldehyde	200	400°F.	500	
50% Diethanolamine	80	680°F.	117	
50% "B stage" phenol-formaldehyde				
Diethanolamine	66.5	700°F.	95	
Diethylene-triamine	16-20	690°F.	23	
Ethylene glycol	150	625°F.	240	

Figure 1

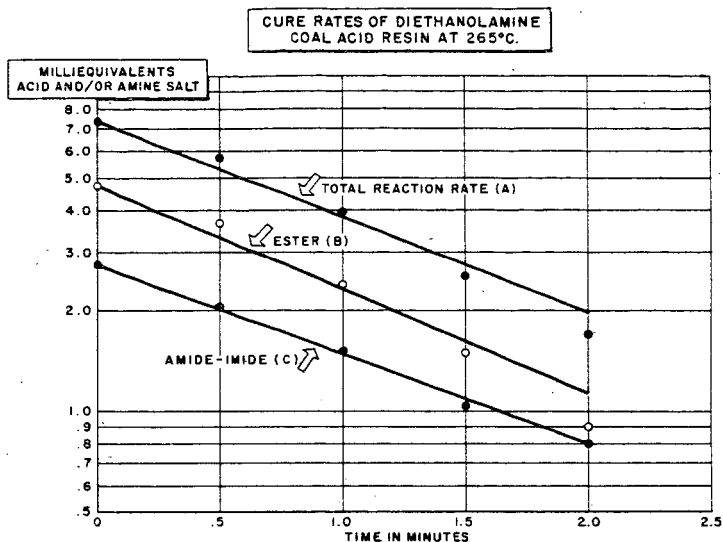


Figure 2

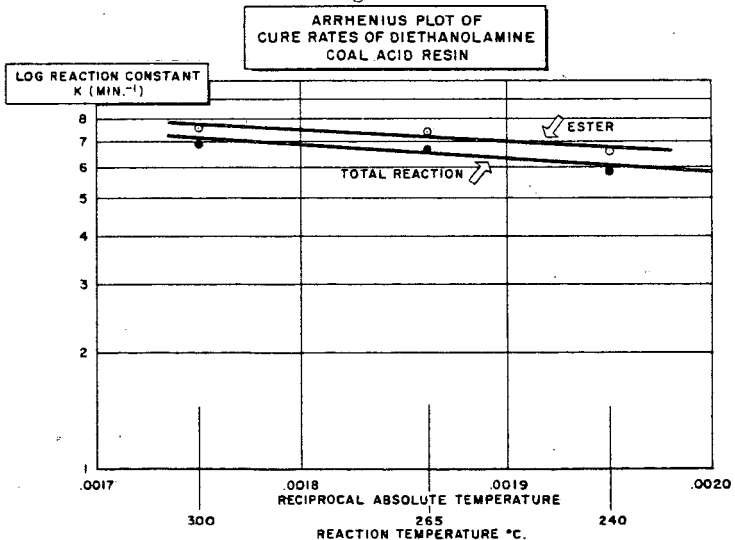


Figure 3

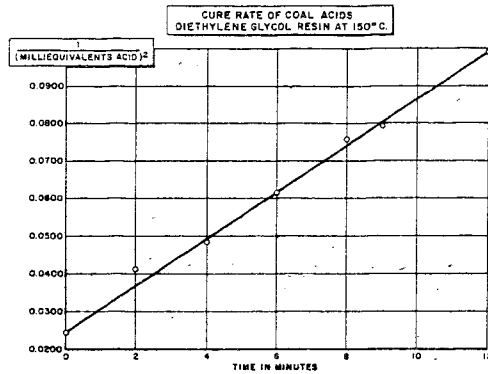


Figure 4

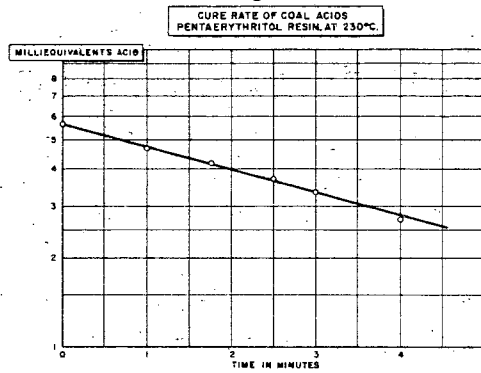
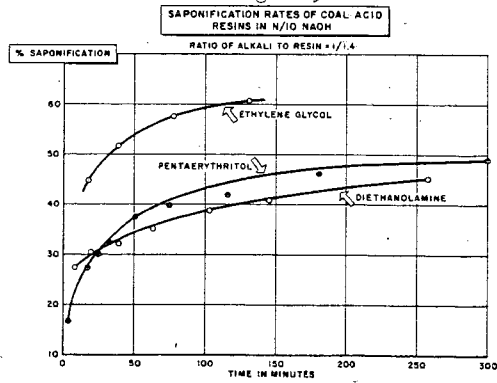


Figure 5



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Coal Acids - Raw Material for Foundry Resins

By

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INTRODUCTION:

Aromatic polycarboxylic acids derived from the controlled oxidation of coal<sup>(1)</sup> have been used to prepare thermosetting resins of interest to the foundry industry. The monoethanolamine, diethanolamine, ethylenediamine, diethylenetriamine and pentaerythritol adducts of these coal acids were investigated as shell molding resin binders.

The current uses of a phenol-formaldehyde resin in the foundry industry illustrated some of the market potentials for the new coal acid resins. The largest market is found in shell molding where some 17 million pounds of phenol-formaldehyde resin was used in 1957. The increased use of the phenol-formaldehyde resin with cereal binders in steel cores is another market with good growth potential.

Sand briquettes bonded with the coal acid resins were tested for tensile strength and the resins of particular interest evaluated in shell molding. The coal acid - pentaerythritol preadvanced resin was outstanding in overall performance as a shell molding binder and thus will be the resin of prime interest in this paper.

Resin Preparation

The resin adducts of interest in this investigation were homogeneous solutions of the coal acids and reactant in water. The coal acid - pentaerythritol resin was partially advanced in water to give a still water soluble homogeneous solution. These water solutions afford an easy and economical method of applying the resin to the sand. In most cases, equivalent ratios of the reactants were used in the resin preparation and resin adduct concentrations of 60-70% gave solutions of workable viscosities. The resins as water solutions have an unlimited storage life.

Requirements of a Shell Molding Resin

The first requirement of a shell molding resin is that it must give a free flowing resin coated sand which on heating thermosets to firmly bond the sand grains together. The resultant shell mold must have sufficient heat resistance to withstand the shock of molten metal and hold close tolerances until the metal has set. At the proper time in the metal set cycle the shell must also burn out to give collapse of the shell and a clean casting. The temperature of collapse can be governed by the resin type and concentration, e.g. urea formaldehyde gives a low temperature collapse for magnesium and aluminum castings. Phenolic resins afford higher heat resistance and are commonly used for malleable iron and steel castings.

The potential resin binder must be effectively and easily dispersed in a sand mix by means of a Simpson or similar type muller. Dry blending of the sand and powdered resin has been popular in the past, but it is rapidly being replaced by a more effective liquid resin coating procedure. In this procedure a source of hot air may be used during the mulling operation to dry the resin coated sand until it is free flowing. Maintenance of this free flowing condition during storage is necessary for optimum pattern performance later.

It is important that the resin binder be cured and thermoset within a reasonable period of time. The approximate time and temperature limits are illustrated in the typical shell molding procedure given below.

- (1) The dry resin coated sand is dropped onto a preheated (400-500°F.) metal pattern and allowed to remain for 15-35 seconds. This time period known as the coat or dwell time determines the thickness of the shell.
- (2) At the end of the proper dwell time the entire pattern is inverted 180 degrees allowing all the excess and unbonded sand to fall back into the dump box. A dough like shell of resin bonded sand is left adhering to the metal pattern.
- (3) The metal pattern and partially cured shell is then placed in an electric or gas furnace (800-1400°F.) where the cure is completed in 40-60 seconds.
- (4) The thermoset shell mold is then ejected from the metal pattern by hydraulically operated ejection pins.

The fabrication performance and pouring behavior of the shell mold is greatly dependent on the shell having sufficient tensile strength at a reasonable resin concentration, e.g. 3.5-5% resin solids. Factors that affect the tensile strength of the resin bonded sand include the resin's actual composition, the efficiency of the coating operation, the degree of resin flow before thermoset and the temperature range necessary for this flow. All of these factors and the conditions necessary for the optimum tensile strength can be evaluated by preparing briquettes from the dried resin coated sands.

#### Preparation of the Coal Acid - Pentaerythritol Resin -(ET-400)

Most of the coal acids used in this work were prepared at the Dow Chemical Company. These coal acids were similar to those made by the Carnegie Institute of Technology (2) and had an equivalent weight of 80-85 and average functionality of approximately three.

The first partially esterified coal acid - pentaerythritol resins were prepared by stirring and refluxing the mixture for a period of 3-6 hours. The degree of advancement was determined by titration of the available carboxylic acid groups. The reaction of a 75% solids solution of 1 equivalent coal acids - 1 equivalent pentaerythritol during the first two hours of reflux is rapid. An equilibrium esterification of 38% was obtained after 8 hours. When 0.9 equivalent of pentaerythritol (75% solids solution) is used an equilibrium esterification of 32% is reached after 8 hours. The effect of solids concentration on the esterification rate is shown by the fact that a 90% solids solution of ET-400-85 (contains 0.85 equivalent pentaerythritol) gives 25% esterification at the end of the first twenty minutes of reflux.

The partially advanced resin is a viscous solution which does not exhibit any precipitation on standing if the advancement is greater than 12%. The resin solution at 60-65% calculated reacted solids gave a very workable viscosity.

#### Physical Properties of the Coal Acid - Pentaerythritol Resins -(ET-400)

Preparation of one quarter inch briquettes from the dried resin coated sand allowed a study of the physical properties of the coated sands as they were related to the resin composition and pretreatment. The sand coating operation was done in a "Kitchen Aid" mixer or in large batches in a Simpson Muller. A source of hot air directed onto the sand mix shortens the time required for the mulling operation. After screening the coated sand through a 42 mesh screen it was dropped into a quarter inch deep briquette mold preheated to 425°F. The coated sand was allowed to stand for 10-15 seconds and then the excess unbonded sand scraped off with a thin metal strip. Curing of the briquette at 650°F. for 2 minutes gave the finished test specimen. These were then tested on a motor driven Dietert Tensile Tester.

A. Optimum Pentaerythritol Concentration in ET-400

Tensile strength determinations have shown that the pentaerythritol concentration can be dropped to 0.9 equivalent pentaerythritol to 1.0 equivalent coal acids without reducing the resin's bonding strength. Use of a 1:1 ratio of hydroxyl to carboxylic acid groups would seem unnecessary since steric hindrance undoubtedly prevents the reaction of some of the carboxylic acid groups.

B. Physical Strength vs. Resin Concentration

A plot of the percent of reacted resin solids on a coarse Ottawa sand vs. the resultant tensile strengths is shown in Figure 1. The briquettes were bonded with an ET-400-9 resin with a preadvancement of 17.5% and cured for 2 minutes at 650°F. A tensile strength of 360 psi. is obtained at the 4% resin level commonly used in commercial shell molds. Naturally, the strength at a certain resin level will vary with the size distribution of the sand, the clay content of the sand, the resin composition and the coating techniques. Each of these factors will be discussed later.

C. Effect of Resin Preadvancement

The tensile strength of the ET-400 resin coated sand has been found to be a function of the resin preadvancement. The preadvancement necessary for optimum tensile strength appears to be in the range of 13-18%. Figure 2 shows the effects of preadvancement on the tensile strengths of two different resin coated sands. This particular data was obtained on small one and a half pound batches of sand coated in a "Kitchen Aid" mixer. The one tensile strength value in Figure 2 marked muller demonstrates that higher tensile strengths may be expected from the more effective coating obtained with a Simpson Muller.

The presence of clay and other nonsilica impurities in the Vasser bank sand could explain the differences in tensile strength of the Vasser bank AFS 100 sand as compared with the high silica content Wedron AFS 116 sand. The clay and silt impurities could indeed decrease the flow of the resin before the thermoset. Thus, flow of the resin coating on a sand grain to the surrounding sand grains and formation of a complete bond would be decreased.

The most important property controlled by resin advancement is the rate and temperature at which the resin flows. The improved flow behavior of the resin on coated sands with less preadvancement is directly reflected in the improved tensile strengths. The temperature at which the resin film on a sand grain will start to flow can be determined and is referred to as the stick point. A lower preadvancement of the ET-400 resin gives a lower stick point and a resultant higher tensile strength.

Preliminary observations have shown that the amount of moisture pickup by the resin coated sand is another factor controlled partially by the degree of resin advancement. Thus, adequate resin advancement is necessary so that the resin coated sand will remain in a free flowing condition before actual use. Sand coated in a Simpson Muller with a resin of at least 15% preadvancement will give a stable free flowing sand. This range of resin preadvancement may also be expected to give nearly optimum tensile strengths.

Shell Mold and Core Fabrication

The ET-400 resin with optimum sand binding properties was then examined in the actual fabrication of shell molds and cores. The small three prong cover plate type shell mold that was prepared on a small dump box machine is shown in Figure 3. Hollow shell cores have also been prepared on a commercial Shalco core blowing machine. Both

pieces of equipment employ the same basic principles of investment, removal of excess unbonded sand and final cure as outlined earlier.

#### A. Sand Coating Procedure

The proper mulling procedure is second only to the resin in determining the final behavior of the coated sand in shell mold fabrication. The resin formulations for actual shell fabrication were applied to 20 pound batches of sand contained in a Simpson Muller.

A typical coating operation for the Simpson Muller is given below:

- (1) Charge 9000 grams of sand and 550 grams of liquid ET-400-9 resin (4% reacted solids on sand) and 20 grams Acrawax (0.22%) to the muller.
- (2) Mull for 1 minute.
- (3) Hot air supply started and continued until coated sand went through the agglomeration stage.
- (4) Mulling continued for an additional 15 minutes with hot air.
- (5) Coated sand dumped and screened through a 40 mesh screen.

The Acrawax serves as a lubricant for the final resin coated sand and helps the sand retain its free flowing character. The hot air for the mulling operation was furnished by a small modified hair dryer with a maximum nozzle temperature of 500°F.

During the agglomeration stage it was found necessary to stop the muller several times and manually break up the plastic like sand mass. Coating of 720 pound batches of Nugent AFS 75 sand with ET-400 in a commercial size muller did not give this problem. The entire cycle from resin addition to coated sand discharge required 14 minutes in the commercial setup. Total time for the coating operation in the small Simpson Muller was 35 minutes.

#### B. Shell Mold Properties

A Nugent AFS 75, coarse Ottawa or Wedron AFS 116 sand coated with 4% of ET-400-9 resin gave good three prong cover plate shell molds at a pattern temperature of 450-500°F., investment time of 15 seconds and cure time of 40-60 seconds. A resin preadvancement of approximately 15% is preferred for maximum tensile strength and pattern performance at a low pattern temperature of 450°F. Moisture stability of the ET-400-9 coated sand appears to be good since no buildup of coated sand on the back side of the shell and/or peel back of a portion of the shell occurs. An excessive amount of moisture also tends to cause the agglomeration of the individual sand particles into units of several particles. These small agglomerates give poor packing of the sand particles at the pattern surface and the resulting poor surface hardness and strength.

The differences in tensile strengths of a high silica sand and bank sand shell mold is again illustrated by the following values. The tensile strength of the 4% ET-400-9 (advanced 16%) coated Nugent sand averaged 315 psi. as compared to the value of 795 psi. for the resin on Wedron sand. Hardness as measured by a Dietert Hardness Tester was 80 for the Nugent shells and 90 for the Wedron sand shells.

Recent work has shown that the addition of a nonionic surfactant, e.g. 0.25% Triton X-100, to the resin coated Nugent or Vasser sand will give a 25% strength increase. Replacement of 30% of the pentaerythritol in the ET-400 resin with a

glycol or ethylene oxide adduct will also give a 25-40% increase in the resin strength. Thus the tensile strength of a modified 4% ET-400-9 coated Nugent sand can be expected to average 400-450 psi.

A field test of the ET-400-9 resin as a shell molding binder has been attempted at a malleable iron foundry. The resin used in this test was one of the earlier ET-400-9 formulations preadvanced to 28.5%. The performance of the resin in the coating of the Nugent sand in 720 pound batches was good. Shell molds of 20 x 30 inches in size were fabricated at a pattern temperature of 500°F., investment time of 34 seconds, and cure time of 50-60 seconds. Figure 4 shows one of the 20 x 30 inch shell molds being ejected from the pattern after cure. Approximately 25 castings weighing 11 pounds a piece were successfully cast without any major metal breakouts. The major point for improvement appeared to be the need for increased tensile strength. Tensile bars prepared from this coated sand gave an average tensile strength of 170 psi. The ability of the newest ET-400 formulation to give some 400 psi. strength on Nugent sand may give the needed additional strength for a completely successful commercial test.

### C. Shell Core Properties

Acceptable commercial hollow shell cores (23 inches in length and 2-5 inches in width) have been fabricated on a Shalco core blowing machine using a 3.5% ET-400-9 coated Wedron sand. The resin had been advanced to 28.5% esterification. Shell cores with excellent hardness (90 on Dietert Tester), detail and strength were prepared at 600°F. with an investment time of 5-15 seconds and cure time of 1.5-2.0 minutes. These conditions correspond to cure conditions used with a commercial phenol-formaldehyde resin coated high silica sand.

### Core Binders

The foundry industry's interest in improved core binders has encouraged the use of the urea formaldehyde and phenolic formaldehyde resins. Principle use of the phenolic resin in solid foundry cores has been limited mostly to steel cores. The need for a more heat resistant binder for steel cores has limited the resin to a phenolic type. The cheaper urea formaldehyde type resin finds wide use in the nonferrous and ferrous type foundries. Both resins are used in conjunction with various cereal flours and core oil binders.

Preliminary data indicates that several of the coal acid type resins may find utility in foundry cores. Specifically, cores with tensile strengths of 570 psi. have been prepared from an Ottawa AFS 60 sand bonded with 1.0% ET-400-9, 1.0% Mogul B211 flour and 5% water. Core mixes of this type have been successfully core blown with commercial machines. The tensile data of other coal acid resins given in the preceding paper also suggests the possible use of these in the core binder application.

Preparation of briquettes from a moist resin coated sand and allowing the briquettes to stand at room temperature leads to the development of considerable green strength. This green strength is the result of the air drying of the resin film to give a "dry" water plasticized resin film surrounding and bonding each sand particle. The diethanolamine resin adduct for example, yields an optimum strength of 325 psi. at a 6% resin concentration while 6% of the diethylenetriamine adduct gives a green strength of 240 psi. after only 20 hours at room temperature. This green strength property could also be of interest in sand core fabrication.

### CONCLUSIONS:

Increasing foundry interest in new synthetic thermosetting sand binders has opened markets for resin binders that have new and improved physical properties. A new type of sand binder for this purpose may be derived from the oxidation products of bituminous



coal. Specifically, thermosetting resins may be prepared from these coal acids and an alkanolamine, polyhydroxyl or polyamine reactant.

The coal acid - pentaerythritol resin (ET-400-9) preadvanced to 13-18% esterification is of particular interest in shell molding work. A 13-18% preadvancement will produce a free flowing sand with optimum tensile strength. Experimental shell molds have been prepared with this ET-400-9 resin at a pattern temperature of 450-500°F., investment time of 15 seconds and cure time of 40-60 seconds. Both high silica content sands and bank sands have been used in the shell mold fabrication. At a 4% resin concentration 315 psi. of tensile strength can be expected with a medium fine, unwashed bank sand. The addition of a surfactant to the resin increases the strength of the resin bonded bank sand to 400 psi. Use of a fine, washed high silica content sand increases the tensile strength to 795 psi.

One attempt to use ET-400-9 as a commercial shell molding binder indicated that a somewhat greater tensile strength is necessary. A new formulation with only 15% advancement may afford the needed strength improvement. Tensile strengths of the original resin bonded sand were 170 psi. as compared to the later tensile strengths of 400 psi. (contains 0.25% surfactant). Commercial shell cores have also been fabricated with ET-400-9.

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2. Franke, N. W., Kiebler, M. W., Ruof, C. H., Sovich, T. R., and Howard, H. C.,  
Ind. Eng. Chem., 44, 2784 - 2792 (1952).

Figure 1

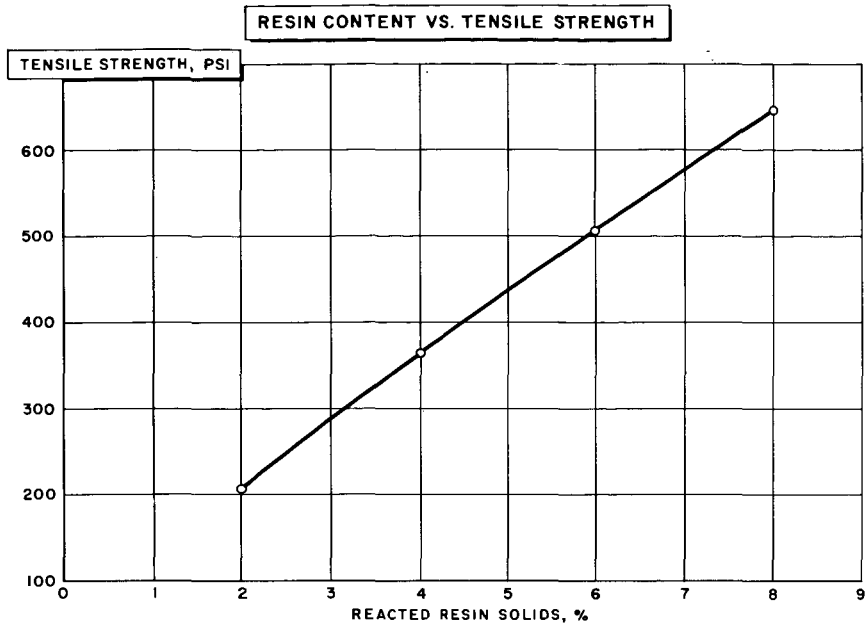


Figure 2

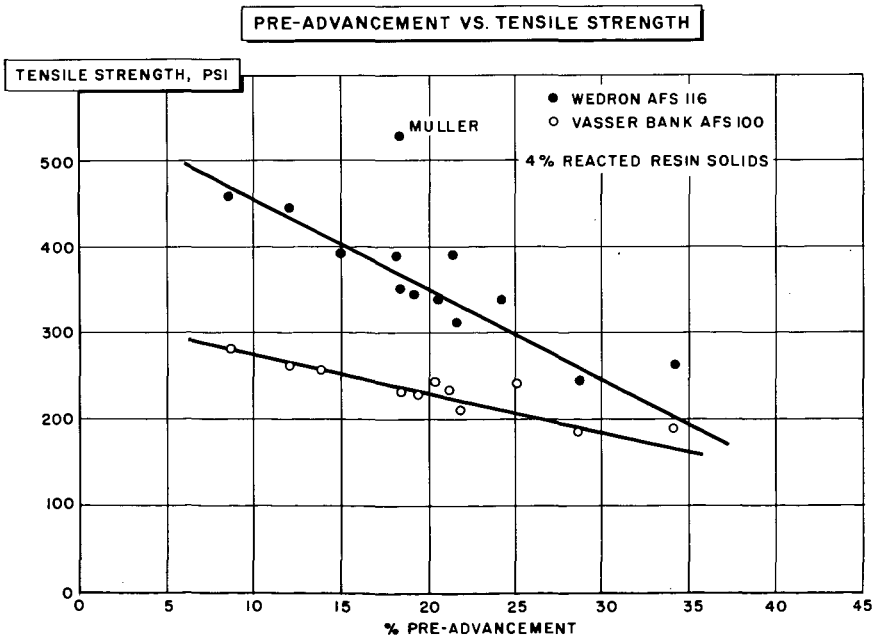


Figure 3

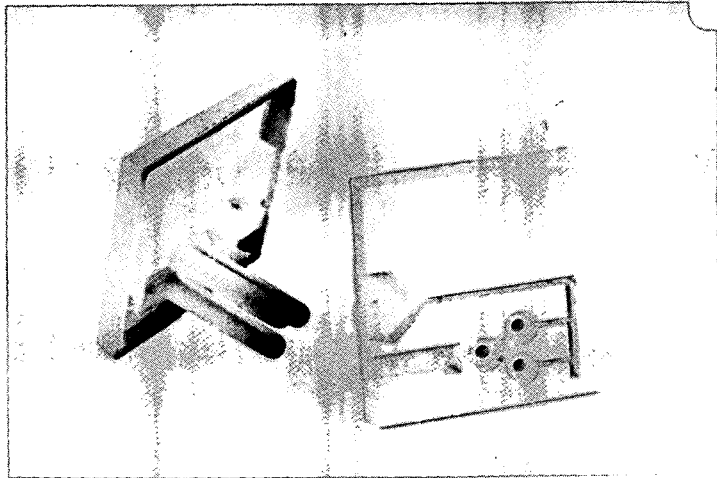
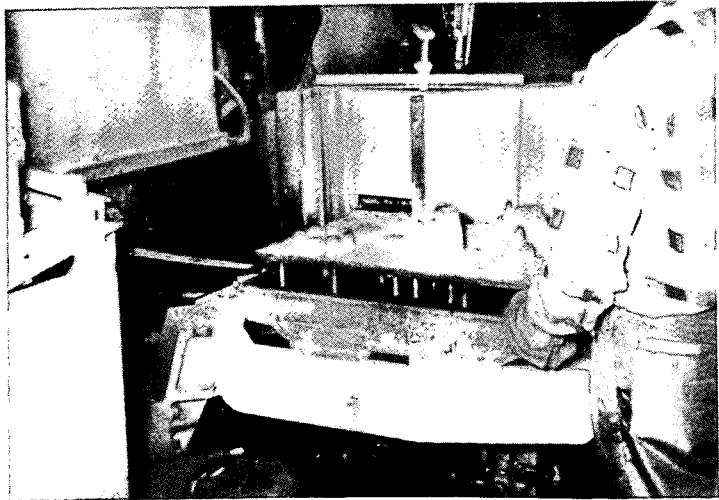


Figure 4



Not for Publication

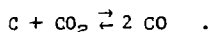
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A Mass Spectrometric Study of the Carbon-Carbon Dioxide Reaction

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INTRODUCTION

Carbon dioxide can react with carbon to form carbon monoxide. This is a reversible reaction which can be represented by the equation



Factors such as the type of carbon used and the impurities present in the carbon can drastically affect the rate of the reaction.

There have been a number of mechanisms proposed for this reaction (1-10). Most of these mechanisms postulate the formation of a surface oxide or complex as an intermediate step in the reaction. There is some agreement that the surface complex does not exist at temperatures above 800°C. and, hence, does not play an important role in the reaction carried out at higher temperatures.

In order to investigate the carbon-carbon dioxide reaction with particular emphasis on the role of any surface oxide intermediate, certain factors must be considered. Since the surface oxide is believed to be unstable at temperatures greater than 800°C., the reaction should be carried out at temperatures as much below this point as possible in order to maximize the probability of surface oxide formation. The amount of gas necessary to completely cover a carbon surface is relatively small (approximately 10 micromoles per square meter for carbon monoxide as the adsorbate (11)). Therefore, the relative change in pressure resulting from the formation of a given amount of surface complex can be maximized by operating at low pressures. A sufficient number of the reaction variables have to be measured to be able to compute a complete material balance throughout the progress of the reaction. Furthermore, the measuring system has to be sensitive enough to detect small amounts of reaction in order to minimize the effect of changing surface area during the course of the reaction.

For this investigation, carbon was reacted with carbon dioxide at temperatures from 400°C. to 700°C. and at starting pressures from 2.7 to 16 microns of mercury. The reaction was followed by monitoring the partial pressures of carbon dioxide and carbon monoxide using a mass spectrometer. The sensitivity of the mass spectrometer was sufficiently great to detect surface coverages of 0.01 per cent and reaction of 0.001 per cent of the carbon in the system.

APPARATUS AND EXPERIMENTAL PROCEDURE

Figure 1 shows a schematic picture of the low pressure reactor. The tubing in the system is  $1\frac{1}{4}$  inches in diameter; the volume of the system is 16.6

liters. The fused silica reactor tube is set at an angle of  $45^\circ$  so that thermal convection will aid in the mixing of the reacting gases. The system can be evacuated to pressures of  $10^{-5}$  mm. Hg using an oil diffusion pump which is connected to the reactor by stopcock  $S_1$ .

There are three pressure measuring devices - an ionization gauge, a thermocouple gauge and a McLeod gauge. Since the mass spectrometer measures partial pressure of all gases present, it also can be used as a pressure measuring device.

The reaction system can be isolated from the mass spectrometer by stopcock  $S_4$ . The reaction gases are admitted to the reaction system through stopcocks  $S_2$  and  $S_3$ .

The carbon sample is placed in a 1 x 5 cm. fused silica tube sealed at one end. The sample container can be lowered into the reaction tube through a sample port in the upper part of the apparatus. The sample container rests on a fused silica tube, which extends upwards from the bottom of the reaction tube. This support tube also contains a chromel-alumel thermocouple. The cap for the upper port in the reactor contains a Pyrex optical-flat window through which the sample can be observed.

The sample is heated by a 1 KW tube furnace which surrounds the reaction tube. The furnace is  $8\frac{3}{4}$  inches long. The temperature of the furnace, as indicated by the thermocouple in the sample support tube, is regulated by an automatic controller-recorder.

The mass spectrometer has been modified so that the reactor can be directly connected to the inlet leak of the spectrometer analyzing tube. Under the conditions used in this investigation, the spectrometer bled off less than two per cent of the total gas present during the course of a run.

A programmed magnetic field controller was constructed to enable the mass spectrometer to sequentially monitor the mass 44 ( $\text{CO}_2^+$ ) ion beam and the mass 28 ( $\text{CO}^+$ ) ion beam every 15 seconds.

In order to determine the time constant of the analyzing system, the reactor was filled with carbon monoxide to a pressure of 8 microns of mercury; and a 5 per cent increment of carbon dioxide was admitted into the reactor. By adjusting the mass spectrometer to monitor mass 44 ( $\text{CO}_2^+$ ), the time taken for the 44 peak to reach a steady state gives an idea of the rate of diffusion and mixing of the gases in the reactor. It was found that the response of the spectrometer was practically instantaneous, with a steady state value obtained within 5 seconds.

The carbon used for this investigation was a highly ground sample of SP-1 spectrographic graphite\*. The spectrographic graphite was ground\*\* for 16 hours

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\* The unground SP-1 sample was supplied by the National Carbon Company.

\*\* The SP-1 sample was ground through the courtesy of Mr. S.B. Seeley of the Joseph Dixon Crucible Company.

in a vacuum ball mill in order to increase its surface area, as described recently by Walker and Seeley (12). After grinding, the area of the graphite wear dust was 560 m.<sup>2</sup>/g. The grinding process introduced ca. 5 per cent iron into the sample.

The carbon sample was heated to a temperature of 850°C. in vacuum for 3 hours prior to each run. This pretreatment insured that the gases evolved upon the heating of the sample at the end of each run were a result of the reaction and not the past history of the carbon.

#### RESULTS AND DISCUSSION

Figure 2 shows typical data obtained from the mass spectrometer during a run. This figure illustrates how the spectrometer is calibrated for carbon monoxide, and carbon dioxide just prior to and immediately after the reaction period. Also it shows removal of the surface complex as carbon monoxide upon outgassing the sample following the reaction.

Figure 3 presents the results of this run after data reduction. The reaction rates could be duplicated to within 5 per cent in runs at the same temperature. It was found that the rate of carbon monoxide formation was slightly less than twice the rate of carbon dioxide consumption. This departure from a two to one ratio involves a small amount of carbon monoxide "tied" to the surface of the carbon sample. This complexed carbon monoxide could be recovered by heating the carbon in a vacuum at higher temperatures after the run.

Figure 4 shows the plots of log carbon dioxide concentration versus time for the reaction over the temperature range 400° to 700°C. The experimental data very closely follow a log function throughout the course of the reaction at all temperatures. This indicates that the rate of reaction of carbon dioxide is first order with respect to the carbon dioxide pressure throughout the entire reaction at all temperatures investigated.

With the experimental conditions used in this investigation, two factors can affect the reaction rate, chemical reactivity and the rate of diffusion of the reacting gas through the unconsolidated carbon sample. When the rate of diffusion is large compared to the rate of chemical reaction, the latter will completely control the over-all rate of reaction. Under these conditions the rate of reaction per unit surface area will not be affected by variation in sample size. However, if the rate of chemical reaction is greater than the rate of internal diffusion, an increase in weight of sample reacted will not have a proportional effect on the over-all rate of reaction. Therefore, the rate of reaction per unit surface area will decrease. It was found that the rate of reaction per unit surface area varied with weight of sample reacted.

Table 1 gives the rate constants\* for the decrease in carbon dioxide pressure with time per unit surface area versus the sample size.

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\* In a constant pressure reaction system or a constant volume reaction system where only a small amount of the total gas is heated, the rate data obtained should be normalized to a constant concentration basis. For this investigation, 27°C. was taken as the standard temperature. Therefore, the experimental rate constants were multiplied by the ratio of the temperature of the reaction to the standard temperature in degrees absolute.

TABLE 1

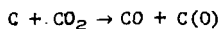
EFFECT OF TOTAL SURFACE AREA OF GRAPHITE WEAR DUST ON THE  
RATE CONSTANT FOR THE DECREASE IN CARBON DIOXIDE PRESSURE IN  
THE REACTION  $C + CO_2 \rightarrow 2 CO$

Temperature °C.	Rate Constant k, sec. <sup>-1</sup> m. <sup>-2</sup> x 10 <sup>6</sup>	
	53 m. <sup>2</sup> Surface Area	133 m. <sup>2</sup> Surface Area
400	1.21	1.12
500	28.7	23.6
650	116.7	89.0

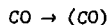
From Table 1 it can be seen that as the reaction temperature decreases the rate constant becomes less dependent on the sample size. This indicates that there was some diffusion control throughout most of the temperature range investigated, with chemical control being almost complete below ca. 450°C. At the lower temperatures, the activation energy approaches a value of 38 kcal./mole.

Figure 5 shows the per cent of the carbon surface that was covered by complex at the end of a reaction versus reaction temperature. It can be seen that the amount of complex formed increases to a maximum in the 600°C. region and then rapidly decreases. The reason for this trend is apparent when one refers to Figure 2. It is noted that in the outgassing of the sample following a run, the complex which has been formed is quite stable until the carbon is heated to temperatures greater than 600°C. The temperature at which the complex was formed was found to have little effect upon its stability.

The carbon monoxide surface complex could be formed as a product of the carbon dioxide reaction:



or it could be due to the chemisorption of carbon monoxide on the surface of the sample,



Here C(O) represents a complex formed upon reaction of CO<sub>2</sub>, while (CO) represents chemisorbed carbon monoxide. By exposing the carbon surface to carbon monoxide, the rate of chemisorption can be studied. It was found that the rate of chemisorption increased to a maximum around 600°C. Table 2 shows the amount of carbon monoxide chemisorbed at 600°C. for various pressures and lengths of time. The coverage of 0.125 per cent of the surface in three days indicates that only a small fraction of the total surface will chemisorb carbon monoxide. The relatively small difference between the amount of surface coverage at a pressure of 2.7 microns of carbon monoxide for 30 minutes and a 24 micron pressure of carbon monoxide for 3 days indicates that the majority of this small area is rapidly saturated with chemisorbed carbon monoxide. The chemisorbed carbon monoxide could be recovered by heating the carbon to temperatures greater than 600°C.

TABLE 2

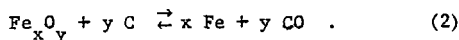
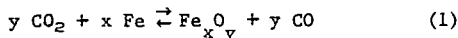
PER CENT OF WEAR DUST SURFACE COVERED WITH CHEMISORBED  
CARBON MONOXIDE AT 600°C.

Time	Pressure, (microns of CO)		
	2.7	8	24
30 min.	0.054	0.065	0.074
3 days	-	-	0.125

Since the chemisorbed carbon monoxide exhibits the same characteristics as the complex formed during the carbon dioxide reaction, it appears that the complex is chemisorbed carbon monoxide. This chemisorption is a side reaction and does not play a role in the mechanism of the conversion of carbon dioxide to carbon monoxide.

It is recalled that, as a result of the grinding process, the carbon sample used in this investigation contained ca. 5 per cent iron. A ground sample from which the iron was removed did not chemisorb any measurable amount of carbon monoxide. The iron had a very strong catalytic effect on the reactivity of the carbon. The "iron-free" sample had to be heated ca. 300°C. higher than the "iron-containing" sample in order to obtain a comparable reactivity. Although the experimental data indicate that the carbon dioxide is converted to carbon monoxide with no measurable build-up of any intermediate products, the great difference in reactivity between the original "iron-containing" sample and the "iron-free" sample indicates that the iron must play an important role in the reaction mechanism.

A possible mechanism by which the iron could catalyze the reaction would be,



Both steps one and two in this mechanism are reversible reactions. The equilibrium constant of step one is pressure independent and is approximately one for the range of temperatures used in this investigation. Step two is a pressure dependent reaction; operation at low pressures of carbon monoxide favors the reduction of the iron. If the rate of the forward reaction in step two is sufficiently fast to prevent a significant build-up of iron oxide, the rate of the back reaction in step one would be small. Under these conditions, only the forward reactions of step one and two would play an important role in the over-all reaction scheme.



#### ACKNOWLEDGEMENT

We wish to express our appreciation to the Mineral Industries Experiment Station of The Pennsylvania State University for supplying the financial support for this research.

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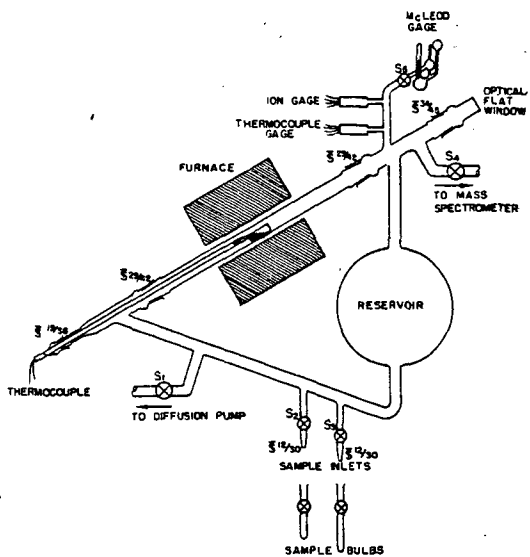


FIGURE 1 - LOW PRESSURE REACTOR

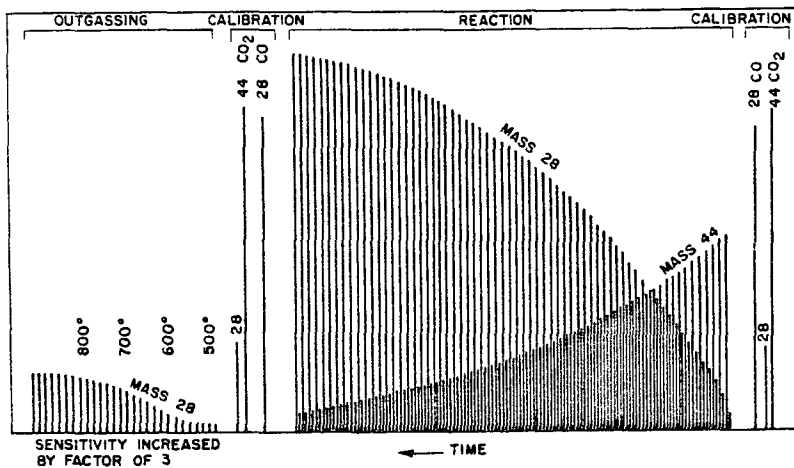


FIGURE 2 - TYPICAL MASS SPECTROMETER RECORD

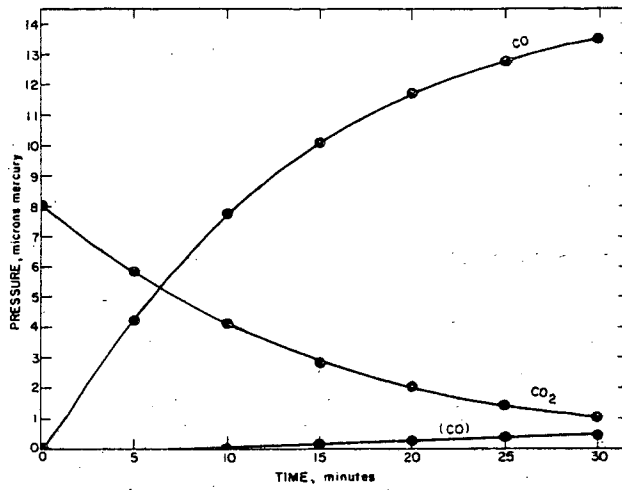


FIGURE 3 - TYPICAL REACTION CURVES

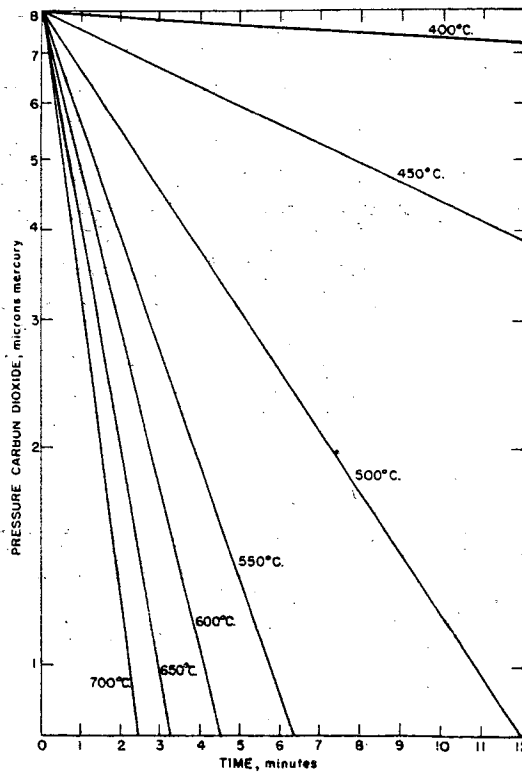


FIGURE 4 - REACTION CURVES FOR GROUND SP-1 GRAPHITE

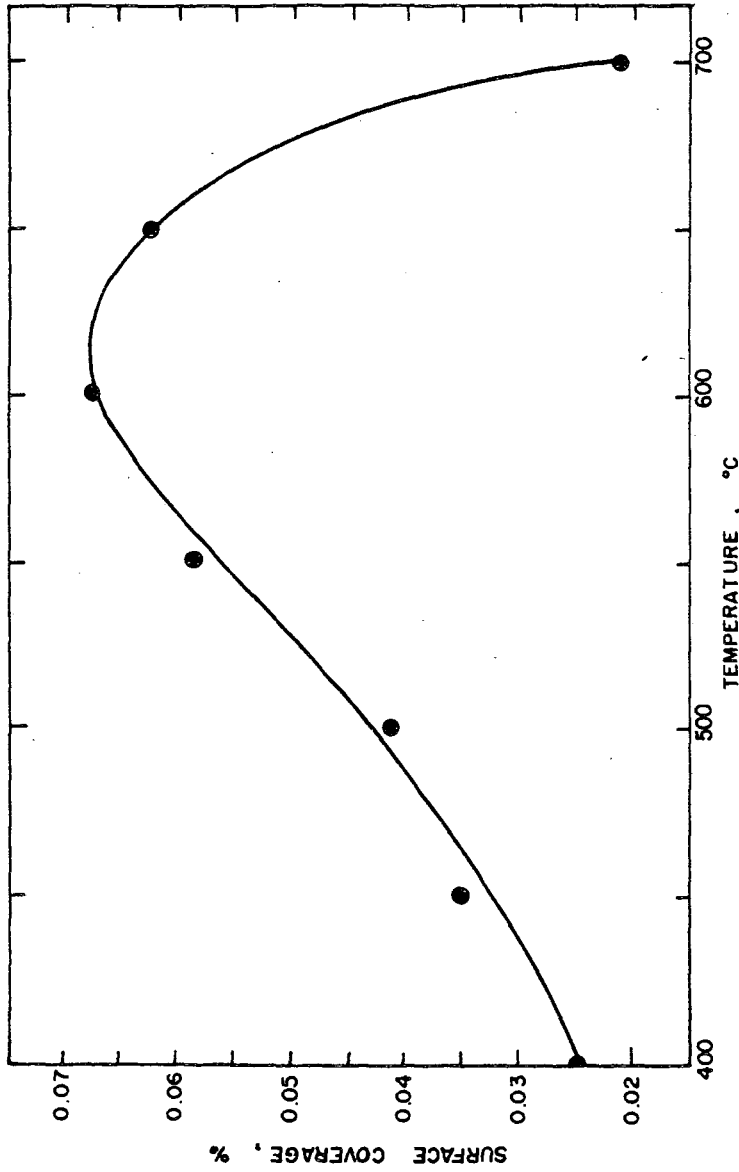


FIGURE 5 - SURFACE COVERAGE OF OXIDE COMPLEX AT END OF REACTION  
VERSUS REACTION TEMPERATURE

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The Impurities in an Acid-Washed 1° Coke-Oven Benzene.  
Concentration of Impurities by Progressive Freezing

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A knowledge of the impurities in an acid refined 1° coke-oven benzene was required for the logical selection of methods for the purification of this product. Surprisingly little definitive information is available on the impurities, other than thiophene and carbon disulfide, in refined coke-oven benzene. Stinzenhöfer (14)\* reported that naphthenes of the methylcyclohexane type prevailed in a residual gasoline fraction obtained in the purification of European coke-oven benzene. Anderson and Engelder (6) prepared a sample of saturated non-benzenoid hydrocarbons from nitration-grade coke-oven benzene by fractional crystallization and fractional adsorption. From the condensation temperatures and refractive indexes of the fractions obtained by efficient distillation of this sample, they inferred the presence of cyclohexane; methylcyclohexane; 3-methylhexane and/or 3-ethylpentane; n-heptane and/or 2,2,4-trimethyl pentane; 1,1-dimethylcyclopentane; and trans-1,2-dimethylcyclopentane and/or trans-1,3-dimethylcyclopentane. A small concentration of toluene was detected, and appreciable concentrations of unsaturated impurities were also indicated. They estimated that the original nitration-grade benzene contained 0.6 volume per cent saturated nonbenzenoid hydrocarbons, 0.004 volume per cent toluene, and 0.1 volume per cent unidentified components.

Anderson, Jones, and Engelder (7) examined the recycle material from the catalytic ethylation of refined coke-oven benzene by the same methods. Any or all of the following paraffins and naphthenes were possible: 2,2-dimethylbutane; 2,3-dimethylbutane; 2-methylpentane; 3-methylpentane; n-hexane; 2,2-dimethylpentane; 2,4-dimethylpentane; 2,2,3-trimethylbutane, 3,3-dimethylpentane; 2,3-dimethylpentane; 2-methylhexane; 3-methylhexane; 3-ethylpentane; n-heptane; 2,2,4-trimethylpentane; cyclopentane; methylcyclopentane; cyclohexane; 1,1-dimethylcyclopentane; trans-1,3-dimethylcyclopentane; trans-1,2-dimethylcyclopentane; cis-1,2-dimethylcyclopentane; cis-1,3-dimethylcyclopentane; and methylcyclohexane. However, the authors observed that some lower-boiling paraffins (2-methylpentane, 3-methylpentane, and n-hexane) appeared to have been introduced during the ethylation process; while most of the naphthenes (except cyclohexane) in the original benzene appeared to have been largely removed. In addition to this serious objection, the inherent limitations of the methods employed in both studies by Anderson and his associates make it virtually impossible, without prohibitive effort, to prove conclusively that any particular compound is present and to measure its concentration accurately.

Kimura and Yasui (11) identified methylcyclohexane and 2,2,4-trimethylpentane in the residue from the commercial chlorination of benzene.

In the present work, the components of virtually the entire impurity content of a conventionally acid-washed 1° coke-oven benzene have been identified positively, and their concentrations have been measured.

\* See References

#### Apparatus

A Perkin-Elmer Model 154-B Fractometer, equipped with a precision temperature controller, was used for the gas-liquid chromatographic separations. Samples were introduced by means of Perkin-Elmer calibrated capillary pipets. The following columns were used:

- (1) Two 2-meter by 0.25-inch-diameter stainless-steel-tubing columns of Perkin-Elmer Corporation "A" material (didecylphthalate on Celite 545, proportions unknown).
- (2) A 25-foot by 0.375-inch-diameter copper-tubing column of polypropylene glycol 2025 (Union Carbide Chemicals Company) on 30-60 mesh Fisher Column Packing in the proportions 31:69.
- (3) A 40-foot by 0.375-inch-diameter copper-tubing column of a mixture of o- and p-benzylbiphenyls on 30-60 mesh Burrell Inert Carrier in the proportions 24:76.

The mass spectrometric analyses were performed with a Consolidated Model 21-103C mass spectrometer.

#### Reagents

All of the pure compounds for calibration of the gas chromatograph and the mass spectrometer were either standard samples from the American Petroleum Institute or research grade materials from the Phillips Petroleum Company.

The benzylbiphenyl was prepared by the procedure of Goldschmidt (10). The particular sample of benzylbiphenyl that was used as the stationary phase in gas-liquid chromatography was a mixture of predominantly the o- with the p-isomer, with a crystallizing point of approximately 65°.

#### Procedure

The benzene selected for this study of impurities was a typical, refined, 1° coke-oven benzene, from the high-temperature carbonization of bituminous coal in modern by-product ovens. This benzene was produced by washing crude benzene-toluene-xylene mixture from coal-tar light oil with 66° Baume sulfuric acid in the conventional manner, neutralizing, and distilling. The benzene had a total distillation range (2) of 79.8 - 80.4 C. Its freezing point (3) was 5.07° C, and its purity (4) was 99.30 mole per cent. Its total sulfur content, determined by a combustion procedure, was 177 ppm. Its thiophene content, determined by the isatin method, was 444 ppm. Its carbon disulfide content by the diethylamine-cupric acetate method was 0.36 ppm. Its bromine index by the proposed ASTM potentiometric titration method was 1.8, which corresponds to 0.00088 mole per cent olefin, if it is assumed that, at worst, all the bromine reacted on an equimolar basis with olefins, and that none reacted with the thiophene. This maximum olefin content is so low that this benzene can be considered to be virtually olefin-free.

Preliminary gas-liquid chromatographic examination of the refined 1° benzene showed that the concentrations of some of the impurities were so small that they must be enhanced to permit certain identification. Schwab and Wickers (13) first introduced the method of progressive or slow fractional freezing for the purification of materials, like benzoic acid, that freeze above room temperature. Dickinson and Eaborn (9) adapted the method to the purification of materials, like benzene, that freeze below room temperature. The principle of either version of

the method is the slow advancement of the solid-liquid interface into the liquid phase. This advancement must be so slow that there is ample opportunity for impurities to be rejected by the freezing solid into the remaining liquid. When most of the sample has frozen, the remaining impure liquid can be removed mechanically, and the purification has been effected. This process requires very simple apparatus and very little effort. The time required compares very favorably with that needed for a careful fractional distillation, and quite small samples can be handled. The efficiency of the purification is impressively high, and the principle is asserted to be superior to zone melting involving a single zone.

If this process can be used to purify a material, then, by the same token, it can be used to concentrate the impurities from that material. To test this argument, part of Dickinson and Eaborn's work was repeated as follows: Approximately 20 ml of thiophene-free ACS-specification benzene was placed in a glass-stoppered test tube, 14 millimeters in internal diameter, 140 mm in length below the tubulure, and approximately 22 ml in volume. This tube, suitably counter-weighted, was lowered by a miniature windlass (driven by an electric clock motor, 1 revolution per hour) at a rate of 3 cm per hour into an ice-water bath maintained at constant level. At the beginning of the experiment, the tip of the tube was touched briefly with a small piece of dry ice to start crystallization and avoid supercooling. Approximately 90 per cent of the sample was frozen after 3 hours. The liquid 10 per cent was withdrawn with a hypodermic syringe, the solid was melted, and the process was repeated until six freezings had been performed. The starting material, the six liquid portions withdrawn, and the final purified material were all subjected to gas-liquid chromatographic analysis on the Perkin-Elmer "A" column at 80.5° C. The chromatogram of the liquid withdrawn after the first freezing displayed six impurity peaks, which were 1.13, 1.50, 4.26, 4.50, 2.17, and 6.04 times as large as the corresponding peaks in the chromatogram of the original benzene. For each liquid portion withdrawn after each successive freezing, the impurity peaks became smaller. The purified material left after the sixth freezing was pure benzene by this test; there were no impurity peaks whatever in its chromatogram. Dickinson and Eaborn's preparation of pure benzene was therefore confirmed, and the application of their technique to the preparation of concentrated impurities is valid. Some time after this work was done, Matthews and Coggeshall (12) also demonstrated the application of progressive freezing to the concentration of impurities from organic compounds.

One obvious extension of the progressive-freezing technique is its application in cascade. For this purpose, a large glass-stoppered test tube (27 mm in internal diameter, 380 mm in length below the tubulure, approximately 230 ml in volume) was substituted for the smaller test tube. This tube, suitably counter-weighted, could be lowered into an ice-water bath, maintained at constant level, by the same windlass arrangement at 5 centimeters per hour. Approximately 90 per cent of a 200-ml sample of the refined 1° coke-oven benzene was progressively frozen in this apparatus in 8 hours. The remaining 20 ml of liquid ("10 per cent off, first pass, first freezing") was withdrawn by syringe and subjected to another progressive freezing in the smaller test tube. Again 90 per cent was frozen and the remaining 2 ml of liquid ("10 per cent off, first pass, second freezing" or "concentrated impurities") was withdrawn. The original refined 1° benzene and the 10 per cent portions withdrawn in the first and second freezings were chromatographed on the polypropylene glycol 2025 column at 121° C. The resulting chromatograms, Figure 1, show the increases in concentrations of impurities that are achieved by cascade operation. In this figure, the three chromatograms have been displaced vertically from each other to a slight extent for the sake of clarity. The encircled numbers designate the various peaks. The attenuation factors are marked near the peaks. In Table I, the heights of the easily measurable impurity peaks in these three chromatograms are tabulated. The first freezing produced a two- to threefold increase in most of the peaks; the second freezing produced a nearly

twofold increase over the first. Cascade operation therefore produced approximately a fivefold increase in most of the peaks. The cascade method was therefore adopted for the production of "concentrated impurities" from the refined 1° benzene.

In view of the extremely small concentrations of some of the impurities in the refined 1° benzene, all the qualitative analyses were performed on the concentrated impurities. The benzylbiphenyl column, originally described by Desty and Whyman (8), was used for all the gas-liquid chromatographic separations, because of its superior resolving power for aromatics and paraffins. This column was operated at 121° C, and 500  $\mu$ l (nominal) of sample was introduced. A typical chromatogram is shown in Figure 2. The very large sample volume was used to supply detectable amounts of the minor impurities, such as those in peaks 1 and 6. To obtain additional information to supplement the chromatographic data, so that qualitative identifications could be made with certainty, each peak in the chromatogram was collected in a trap cooled in liquid nitrogen. The contents of each trap were then analyzed by mass spectrometry. In each case, the mass spectrum of the contents of the trap was first corrected for the very small contribution of the "column blank"--the very small amount of the stationary phase and/or its decomposition products that is vaporized constantly from the chromatographic column and is caught in the trap when it is cooled. The hydrocarbon-type analysis developed originally by Brown (5) was next applied to each mass spectrum to facilitate its interpretation. When the relative retention volume for a chromatographic peak was used to narrow the choice of possible components contributing to that peak, it was then usually rather simple to confirm or reject each of the possible components from the mass spectrum. The relative retention volumes of a small number of pure hydrocarbons were determined under the conditions prevailing in the qualitative analysis, that is, on the benzylbiphenyl column at 121° C, "flooded" with 500  $\mu$ l of benzene. From these data and the published values for a large number of compounds at 78.5° C (8), the relative retention volumes at 121° C for these compounds could be estimated with sufficient accuracy for the preliminary qualitative analyses. Once the presence of a compound had been established by the preliminary chromatographic and mass-spectrometric data, its presence was further confirmed by direct experimental measurement of its relative retention volume on the benzylbiphenyl column at 121° C, "flooded" with 500  $\mu$ l of benzene. Similarly, published mass spectra (1) were used for the preliminary interpretations, but once the presence of a compound had been thus established, its mass spectrum was determined by direct experimental measurement with the Model 21-103C spectrometer. The qualitative compositions of the substances producing the peaks in the chromatogram in Figure 2 are shown in Table II. As more than one compound contributed to each impurity peak and as progressive freezing affected the concentrations of the compounds contributing to any peak to different unknown extents, it was obviously necessary to perform the quantitative analysis directly on the original 1° benzene.

The quantitative analyses were performed by collecting quantitatively in a cold trap the substance producing each peak in the gas chromatogram of a known amount of the original 1° benzene (similar to Figure 2, but with smaller impurities peaks). The time intervals marked above the chromatogram in Figure 2 are identical with those used in the trappings for the quantitative analyses. The entire contents of the trap were then admitted to the mass spectrometer and analyzed quantitatively. Since the concentrations of the several impurities varied over a very wide range, not all of the peaks could be trapped from a single sample of the 1° coke-oven benzene. The amount of sample used in each case is shown in Table II. For a very minor impurity, 500  $\mu$ l (nominal), which is the practical maximum accommodated by the chromatographic column, would provide too small an amount of impurity for spectrometric analysis. In that case, a sufficient number of 500- $\mu$ l (nominal) portions of the 1° benzene was chromatographed in succession to supply the necessary amount of impurity for the spectrometric analysis. When the desired chromatographic peak appeared in each chromatogram,



the same collecting trap was applied to the vent line of the chromatograph until the necessary total amount of that impurity had been collected.

Because this whole procedure can be no more accurate and precise than the quantitative operation of the cold traps, these were studied carefully. The first traps used were simple U-shaped lengths of capillary tubing 2 mm in internal diameter and 18 inches in length, provided with vacuum stopcocks near each end and a standard taper joint at one end (8). Six such traps were used with a manifold arrangement connected to the vent line of the chromatograph. The possibility of absorption of minor components by stopcock grease and occasional plugging of the capillary by frozen condensate led to the adoption of a simpler system, which was used for all the final quantitative analyses. A short glass Y-tube was butted against the end of the vent line of the chromatograph. The butt joint was held in place with Tygon tubing. The traps were of the conventional concentric tube design, 175 mm long, with the inner tube 6 mm in external diameter and the outer tube 16 mm in external diameter. The inner tube ended 15 mm above the bottom of the outer tube. One of these traps was connected to each arm of the Y-tube with a section of Tygon tubing just long enough to permit the application of a hosecock clamp. A drying tube filled with Ascarite was connected with a similar short length of Tygon tubing and clamp to the exit tube of each trap to minimize back-diffusion of moisture and carbon dioxide into the trap when it was chilled. Each trap was purged at room temperature with helium before use. As there were no stopcocks in the system, grease was eliminated. By connecting the traps to the Y-tube and manipulating the clamps at the proper times, any peak could be collected in a trap. Although this arrangement was not quite as fast or convenient as the manifold with stopcocks, it did eliminate the possibility of partial loss of components by absorption in stopcock grease. The traps were immersed to only about one-half to two-thirds of their length during use. As soon as the trapping was completed, the liquid nitrogen level was raised so that the entire length was immersed. By this procedure, loss of trapped material by warming of condensate in the upper part of the trap should be eliminated. The trap was butted to the mass-spectrometer inlet system with Tygon tubing, and its entire contents were analyzed quantitatively in the usual way.

The performance of this entire procedure was tested by introducing known amounts of pure compounds or known mixtures into the gas chromatograph, collecting the components in the chilled traps connected to the chromatograph vent line, and measuring the amounts collected by mass spectrometry. Pure n-heptane was used first. In seven tests, the recovery achieved was 80, 94, 114, 106, 109, 108, and 101 per cent of the amount introduced. A mixture comprising 62.7 volume per cent n-heptane and 37.3 volume per cent cyclohexane (mass spectrometric analysis) was tested next. Each component was trapped individually. In duplicate tests, 108 and 108 per cent of the heptane and 101 and 101 per cent of the cyclohexane introduced were recovered. From these data, the apparent recovery achieved with the procedure might be estimated at  $100 \pm 10$  per cent, although, for reasons unknown, recoveries outside these limits, particularly on the low side, may be observed occasionally.

Positive errors (recoveries higher than 100 per cent) may be caused by 1) excess liquid sample clinging to the outer surfaces of the capillary pipette with which samples are introduced into the gas-liquid chromatograph, and/or 2) error in the calibration of the very small capillary pipette (0.5  $\mu$ l) with which pure liquids are introduced into the mass spectrometer for calibration. The first error is variable; the second is constant. The first error was minimized by touching only the very tip of the pipette to the surface of the liquid sample, removing the pipette from contact with the liquid, and waiting perhaps 15 seconds before introducing the sample into the chromatograph. By this procedure, the excess liquid is minimized at the outset, and the very small excess that cannot

be avoided has time to evaporate. The second error is caused by the difficulties during calibration of filling with mercury the very tiny volume of the mass spectrometer pipette and emptying it completely. Beyond exercising the utmost care in all the manipulations and replicating the calibration with good repeatability, the authors know of no obvious improvement.

Negative errors (recoveries lower than 100 per cent) may be caused by 1) failure to introduce the entire sample into the chromatograph, 2) less than quantitative trapping, and 3) losses in introducing the trapped sample into the mass spectrometer. Gross errors of the first kind can be detected immediately by variations in the peak heights in the chromatogram, and the test can be rejected. The second error is difficult to isolate and study. Packing the trap or increasing the contact of the vapor with the trap walls in other ways might increase the efficiency of trapping, but might also make it more difficult to vaporize all the condensate into the mass spectrometer or to clean the trap for reuse. The third error was minimized by eliminating stopcock grease from the spectrometer inlet system by butting the trap to it with Tygon tubing.

Two special modifications of the standard concentric cylindrical traps were made. When peak No. 9 (Figure 2), the small peak on the long tail of the very large peak No. 8, was trapped, sizable amounts of the material of peak No. 8 were collected and plugged the ordinary trap. A special trap was therefore made to avoid this difficulty, with the external tube 24 mm in outside diameter and 115 mm long, and the internal tube 15 mm in outside diameter and 100 mm long. This trap was amply large to accommodate all the material collected. When peak No. 8 was collected, this trap was still large enough, but in this case it was desirable to introduce the collected material into the mass spectrometer as a liquid. For this reason, a small tip, 8 mm in diameter and 35 mm long, was blown into the bottom of one of the special traps. After the material from peak No. 8 had been collected in this trap, the frozen condensate was melted into the small tip, which was then broken off to make the liquid available.

All the quantitative analyses were performed in duplicate at least. In view of the fact that those errors (described above) that are most difficult to control all tend to cause less than quantitative recoveries, replicate analyses that gave low results were regarded with suspicion and repeated.

#### Results and Discussion

The qualitative and quantitative analyses of the mixtures producing each of the ten peaks in the chromatogram of the 1° coke-oven benzene on the 40-foot benzylbiphenyl column at 121° C are tabulated in Table II. In every case, the residual mass spectrum remaining after the contributions of these components had been calculated was examined. For peaks No. 1, 2, 3, 4, 5, 8, 9 and 10, these residuals were within the expected mass spectrometric error, that is, no residual peak was larger than 3 per cent of the largest peak in the mass spectrum and was usually appreciably less. For these mixtures, it is highly probable that no additional components (beyond those listed in Table II) would be identified at concentrations exceeding approximately 0.005 mole per cent (in each mixture) in any more exhaustive investigation. For peak No. 7, the largest residual mass peak was 4.3 per cent of the height of the largest peak in the spectrum. Moreover, residual peaks occurred at masses 43, 57, 69, 71, 85 and 97, which were 3 to 4 per cent of the height of the largest peak. It is highly probable that some unidentified alkanes and/or naphthenes, present at a total concentration of less than approximately 0.03 mole per cent, account for these peaks. This is approximately 4 per cent of the total 0.70 mole per cent impurity determined cryoscopically.

The type analysis calculated from the mass spectrum of peak No. 6 showed 86 per cent naphthenes and 13 per cent alkanes, with an average carbon number of 8. From the mass spectrum, the naphthene is very probably a trimethylcyclopentane. The specific isomer could not be identified, however, because only six of the possible eight geometric isomers of trimethylcyclopentane (excluding stereoisomers) have been prepared in the pure state and their mass spectra published. The relative retention volume of peak No. 6 also confirms the hypothesis that the naphthene is a trimethylcyclopentane. The impossibility of identifying the naphthene specifically also makes it impossible to identify the accompanying alkane specifically. From the mass spectrum and the relative retention volume, the alkane is very probably an octane. The estimates of the concentrations of the naphthene and the alkane were made from average published values for the mass spectrometric sensitivities for trimethylcyclopentanes and octanes, respectively. These are only estimates, but peak No. 6 in any case accounts for only about 1.5 per cent of the total impurities.

Appreciable concentrations of impurities might be obscured by the very extensive benzene peak (similar to peak No. 8, Figure 2). The material producing this peak was therefore collected and analyzed as previously described. This material was benzene of even higher purity than the benzene of 99.93 mole per cent purity that was used for calibration. The probability of any appreciable concentration of impurities being obscured by the benzene peak is therefore slight.

The chromatograms of "concentrated impurities" on the polypropylene glycol 2025 (Figure 1) and the benzylbiphenyl (Figure 2) columns exhibited three and one peaks, respectively, arriving before peak No. 1. As the total concentrations of the component(s) producing these peaks are very probably appreciably less than one part per million, no attempt was made to collect and identify them.

It can be seen from Table II that most of the 2-methylhexane was found in peak No. 2, but that a small amount was also found in peak No. 3. This is a direct consequence of the fact that the 2-methylhexane had not been completely eluted with the other components of the first peak, before the components of the second peak of the pair began to elute. Similarly, most of the n-heptane was found in peak No. 4, but a small amount was found in peak No. 5. However, as long as both peaks of each pair are trapped from the same sample introduction, no error is caused by this partial failure to resolve the components. This procedure was followed in each of these cases.

In Table III, therefore, the qualitative and quantitative analyses of the impurities have been tabulated on a cumulative basis, without regard to the distribution of a component between two peaks. The concentrations are expressed as volume, weight, and mole per cent, all based on the whole benzene sample. A total of 20 impurities was identified -- 8 alkanes, 8 naphthenes, 1 aromatic, and 1 heterocyclic compound with certainty; and 1 alkane and 1 naphthene with good probability. Neither olefins nor carbon disulfide were detected, as was expected from their very low concentrations. The 501 ppm thiophene determined here agrees fairly well with the 444 ppm found by the isatin method. The average 4.4 per cent of the impurities unaccounted for agrees well with the approximately 4 per cent unaccounted for in peak No. 7.

For all the specifically identified components present in concentrations exceeding 0.007 mole per cent (1 per cent of the total impurity), the average repeatability of the determinations was  $\pm 3.9$  per cent; the worst repeatability was  $\pm 9.9$  per cent. For all the specifically identified components present in concentrations less than 0.007 mole per cent, the average repeatability was  $\pm 8.3$  per cent; the worst repeatability was  $\pm 24.2$  per cent. Over-all repeatability, calculated from the total impurities found, was  $\pm 2.7$  per cent. The accuracies

of individual analyses cannot be estimated; in fact, the only indication of accuracy is the total average recovery, 95.6 per cent of the total impurity measured by the cryoscopic method, which is usually highly accurate for a sample of this kind.

The occurrence in coke-oven benzene of 2,2-dimethylpentane; 2,4-dimethylpentane; 2-methylhexane; 3,3-dimethylpentane; 2,3-dimethylpentane; 3-methylhexane; 3-ethylpentane; 1,trans-2 dimethylcyclopentane; 1,trans-3 dimethylcyclopentane; and 1,cis-2 dimethylcyclopentane, which had been identified tentatively by Anderson and his associates (6, 7), has now been established definitely. 1,trans-2, cis-4 trimethylcyclopentane has been identified in coke-oven benzene for the first time. (The occurrence of another trimethylcyclopentane is highly probable.) Eleven new products of the high-temperature carbonization of bituminous coal have therefore been established with certainty.

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Table I  
Enhancement of Concentrations of Impurities in 1° Coke-Oven Benzene  
by Cascade Application of Progressive Freezing

Peak Number (Figure 1)	Chromatogram Peak Height, arbitrary units		
	Original 1° Benzene	"10% Off, First Pass, First Freezing"	"10% Off, First Pass, Second Freezing" "Concentrated Impurities"
1	0.2	0.7	1.7
2	9.6	25.7	53.6
3	13.4	35.4	74.2
4	47.4	124	251
5	20.2	53	99
6	--	--	3.7
7	2	8	19
9	--	4.3	6.0
10	0.4	1.0	2.8

Table II

Qualitative and Quantitative Analyses of the Individual Peaks in the  
Gas-Liquid Chromatogram of 1° Coke-Oven Benzene

Peak No. (Figure 2)	Total Volume of Sample, μl	Component	Analysis, Mole % Based on Benzene Sample		
			Trial 1	Trial 2	Average
1	1514.4	2,2-dimethylpentane	0.000130	0.000116	0.000123
		2,4-dimethylpentane	0.000747	0.000454	0.000601
2	1009.6	2-methylhexane	0.0231	0.0221	0.0226
		3,3-dimethylpentane	0.000870	0.000827	0.000849
		methylcyclopentane	0.00597	0.00599	0.00598
3	1009.6	2-methylhexane	0.000308	0.000425	0.000367
		methylcyclopentane	0.000671	0.000648	0.000659
		2,3-dimethylpentane	0.0156	0.0134	0.0145
		3-methylhexane	0.0251	0.0232	0.0242
4	169.4	n-heptane	0.0880	0.0844	0.0862
		1,1-dimethylcyclopentane	0.00697	0.00682	0.00690
		3-ethylpentane	0.00523	0.00406	0.00465
5	169.4	n-heptane	0.00490	0.00529	0.00510
		cyclohexane	0.0644	0.0613	0.0629
		1,trans-2 dimethylcyclopentane	0.0550	0.0447	0.0499
		1,trans-3 dimethylcyclopentane	0.0448	0.0487	0.0468
6	1514.4	a trimethylcyclopentane (?)	~ 0.00690	~ 0.00950	~ 0.00820
		an octane (?)	~ 0.0010	~ 0.0010	~ 0.0010
7	169.4	methylcyclohexane	0.229	0.214	0.222
		1,cis-2 dimethylcyclopentane	0.0196	0.0181	0.0189
		1,trans-2,cis-4 trimethylcyclopentane	0.00744	0.00677	0.00711
8	169.4	benzene	Pure benzene		
9	169.4	benzene		0.4777	
		thiophene	0.0466	0.0465	0.0466
10	1009.6	benzene	0.0862	0.0959	0.0911
		toluene	0.0330	0.0338	0.0334

Table III

Qualitative and Quantitative Analyses of the Impurities in  
1° Coke-Oven Benzene

Peak No. (Figure 2)	Normal Boiling Point of Pure Component, °C	Component	Analysis, Based on Benzene Sample				
			Mole Per Cent		Average		
			Trial 1	Trial 2	Mole %	Vol %	Wt %
1	79.205	2,2-dimethylpentane	0.000130	0.000116	0.00012	0.00021	0.00016
	80.51	2,4-dimethylpentane	0.000747	0.000454	0.00060	0.0010	0.00077
2 & 3	90.05	2-methylhexane	0.0234	0.0225	0.0230	0.0381	0.0295
	86.071	3,3-dimethylpentane	0.000870	0.000827	0.00085	0.0014	0.0011
	71.812	methylcyclopentane	0.00664	0.00648	0.00656	0.0083	0.0071
	89.79	2,3-dimethylpentane	0.0156	0.0134	0.0145	0.0235	0.0186
	91.95	3-methylhexane	0.0251	0.0232	0.024	0.039	0.031
	98.428	n-heptane	0.0929	0.0897	0.0913	0.150	0.117
4 & 5	87.84	1,1-dimethylcyclopentane	0.00697	0.00682	0.0069	0.010	0.0087
	93.468	3-ethylpentane	0.00523	0.00406	0.0047	0.0075	0.0060
	80.738	cyclohexane	0.0644	0.0613	0.063	0.077	0.068
	91.87	1,trans-2 dimethylcyclopentane	0.0550	0.0447	0.050	0.063	0.054
	90.77	1,trans-3 dimethylcyclopentane	0.0448	0.0487	0.047	0.060	0.051
6		a trimethylcyclopentane (?)	~0.0069	~0.0095	~0.0082	~0.014	~0.012
		an octane (?)	~0.0010	~0.0010	~0.0010	~0.0018	~0.0015
7	100.934	methylcyclohexane	0.229	0.214	0.222	0.319	0.279
	99.53	1,cis-2 dimethylcyclopentane	0.0196	0.0181	0.019	0.027	0.024
	109.28	1,trans-2,cis-4 trimethylcyclopentane	0.00744	0.00677	0.0071	0.012	0.010
9	84.1	thiophene	0.0466	0.0465	0.0466	0.0411	0.0501
10	110.623	toluene	0.0330	0.0338	0.0334	0.0396	0.0392
Total			0.685	0.652	0.670	0.933	0.808
% of the total 0.70 mole % impurity accounted for			97.9	93.1	95.6		
% of the total 0.70 mole % impurity unaccounted for			2.1	6.9	4.4		

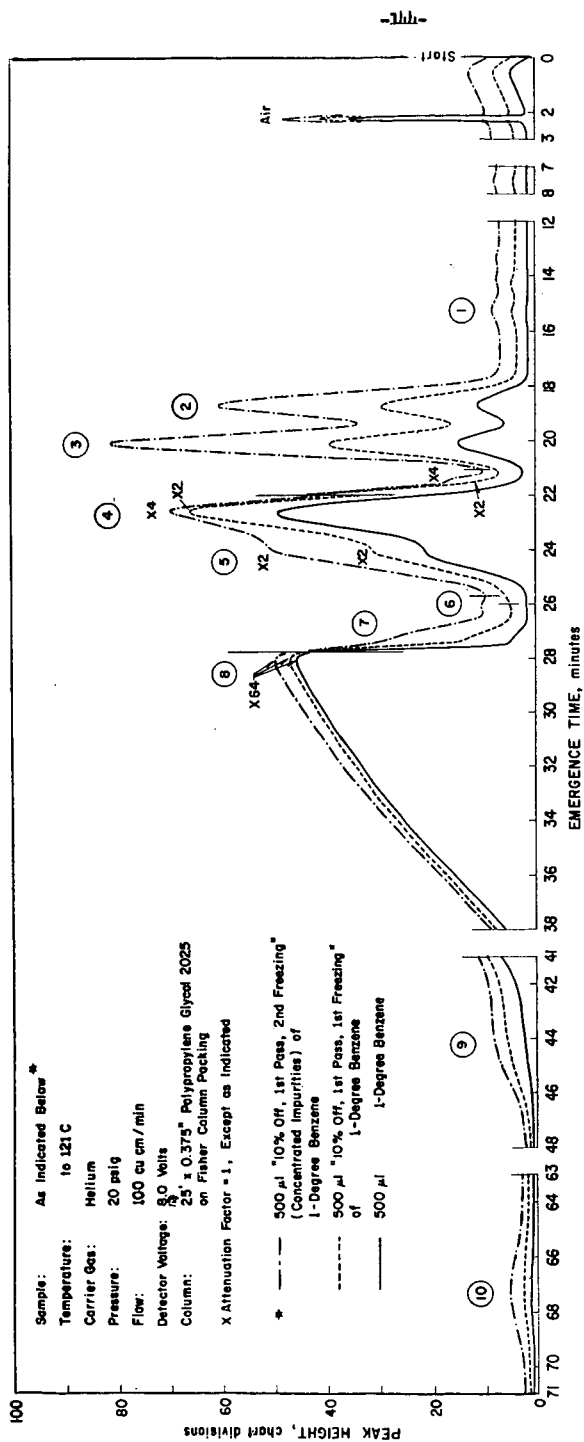


Figure 1. Gas-Liquid Chromatograms Showing Enhancement of Concentration of Impurities in 1-Degree Benzene



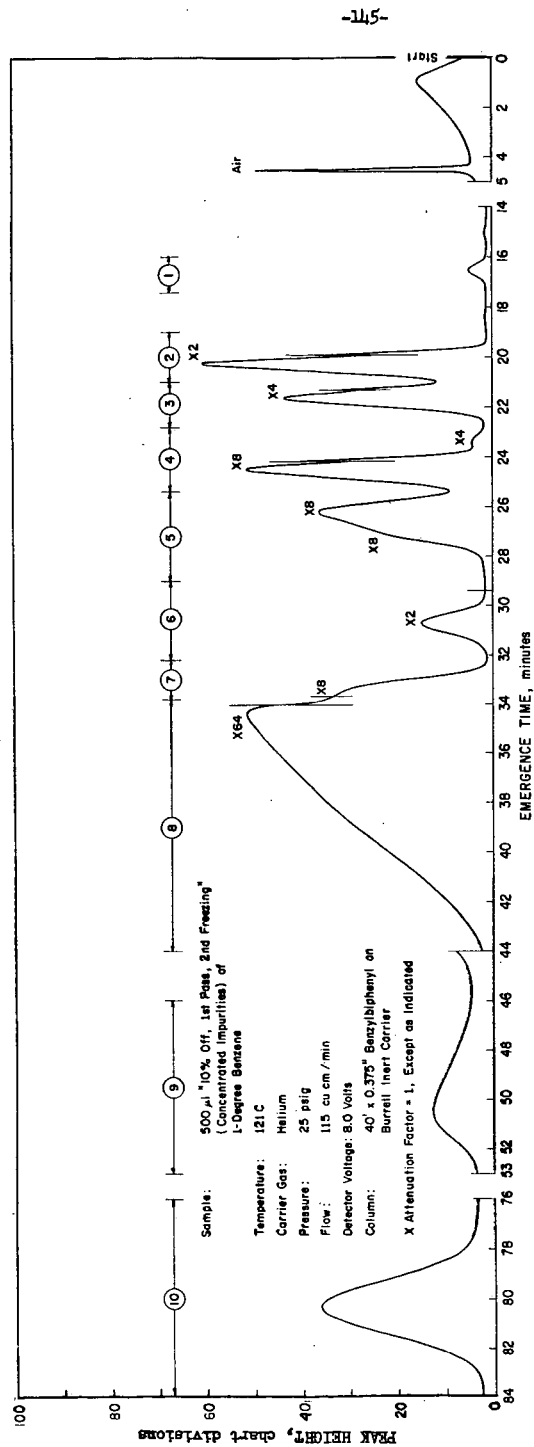


Figure 2.: Gas-Liquid Chromatogram of Concentrated Impurities From 1-Degree Benzene